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NITROGEN TETROXIDE CORROSION PRODUCTS

FINAL REPORT

Chemical and Material Sciences
Research Division of Rocketdyne
A Division of North American Rockwell Corporation
6633 Canoga Avenue, Canoga Park, California

Technical Report AFRPL-TR-69-114

February 1969

**Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command
United States Air Force**

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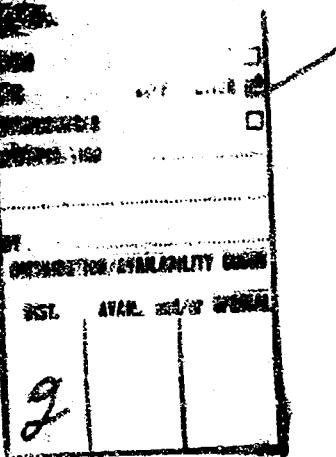
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Air Force Rocket Propulsion Laboratory
Research and Technology Division
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United States Air Force



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FOREWORD

The research reported herein was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California, under Contract F04611-68-C-0070. The monitoring agency was AFPL; the contract monitor was Mr. R. Biggers.

This program was conducted by members of Chemical and Material Sciences, Rocketdyne Research Division.

Dr. E. F. C. Cain (Manager, Engineering and Analytical Chemistry) served as Program Manager and Responsible Scientist. Contributing personnel were Dr. F. C. Gunderloy, Jr. (Principal Scientist, General and Polymer Chemistry), Dr. J. E. Sinor (Principal Scientist, Engineering Chemistry), Dr. R. I. Wagner (Member of the Technical Staff, General and Polymer Chemistry), and Mr. M. J. Stutsman (Member of the Technical Staff, Engineering Chemistry).

This report contains no classified data abstracted from other reports. It has been assigned the Rocketdyne Report No. R-7789.

This report has been reviewed and is approved for publication.

W. H. ESHKE, Colonel, USAF
Chief, Propellant Division
Air Force Rocket Propulsion
Laboratory

ABSTRACT

Study of the phenomenon of flow decay, begun on earlier programs, was continued with a change to MSC PPD-2A propellant (N_2O_4 + 0.6 percent NO). Flow decay occurs with this propellant, even when dry (less than 0.1-percent water equivalent), as a result of deposits of the solid corrosion product, $NOFe(NO_3)_4$. It was found that the presence of excess water in amounts up to the general use limit of 0.2 percent changed the characteristics of the deposits formed when nitrogen tetroxide is heated, then cooled prior to or during flow. Instead of the crystalline solid ($NOFe(NO_3)_4$) which is deposited from dry propellant, gelatinous or viscous liquid phases are formed in wet propellant.

The appearance of these deposits is governed by an equilibrium solubility limit similar to that observed for the solid deposits in dry propellant. The gelatinous or viscous liquid deposits were not observed to adhere to and plug valves and orifices, as does $NOFe(NO_3)_4$, but they did clog filters. Chemical additives previously shown to be effective in dissolving and eliminating $NOFe(NO_3)_4$ were not effective against the deposits obtained from wet propellant. Traces of aluminum and titanium were detected in flow decay deposits obtained from flow systems with aluminum and titanium tanks.

CONTENTS

Foreword	ii
Abstract	iii
Phase I: Laboratory Testing	1
Introduction	1
Experimental System	2
Laboratory Depositor	2
Results and Discussion	4
Deposition of Solid Flow Decay Material	4
Deposition of Liquid Flow Decay Material	8
Additive Effectiveness and Life	12
Effect of Water Equivalent Concentration on $\text{NOFe}(\text{NO}_3)_4$	23
Attempted Removal of Chloride From N_2O_4	29
Analyses for Water Equivalent Concentration in N_2O_4	32
Phase II: Engineering Evaluation	35
Introduction	35
Experimental System	35
Flow Bench	35
Instrumentation	37
Operating Procedures	37
Results and Discussion	38
Flow Decay With Dry Propellant	38
Effect of Water	42
Filter Effects	47
Additive Effects	53
Coupon Corrosion Tests	58
Flow Decay in Aluminum and Titanium Systems	59
Conclusions and Recommendations	65
The Basic Chemistry of Flow Decay	65
Physical Manifestations of Flow Decay	66
The Prevention of Flow Decay	67
Purification and Analysis of Nitrogen Tetroxide	69
Flow Decay and Corrosion of Nonferrous Metals	70
References	71

ILLUSTRATIONS

1. Laboratory Depositor Schematic	3
2. Liquid-Solid Mixture Flow Decay Deposit	11
3. Experimental Flow Bench	36
4. Flow Decay and Cleanout in Valves With PPD-2A Propellant	41
5. Effect of Water	45
6. Flow Decay and Temperature Reversal in Filters With Wet N_2O_4	46
7. Flow Decay and Cleanout in Filters With Dry N_2O_4	48
8. Flow Decay in Two Filters With Wet N_2O_4	50
9. Flow Decay in Filters With Wet Propellants	52
10. Flow Decay With Picric Acid Additive	54
11. Effect of Dimethylsulfoxide on Flow Decay	57
12. Aluminum, Titanium, and Stainless-Steel Parallel Flow System . .	60
13. Flow Decay in Aluminum, Titanium, and Stainless Steel	62

TABLES

1. Deposition of $\text{NOFe}(\text{NO}_3)_4$	6
2. Analysis of Propellant	7
3. Deposition of Liquid Flow Decay Material	9
4. CuK_α X-Ray Diffraction Powder Data of $\text{NOFe}(\text{NO}_3)_4$ Before and After Exposure to Green N_2O_4	13
5. Composition of Additive- N_2O_4 Solutions	15
6. Additive Effectiveness and Life	16
7. Interaction of $\text{NOFe}(\text{NO}_3)_4$ With Green N_2O_4 of Various Water Equivalent Concentrations	25
8. Preparation and Analysis of N_2O_4 -NO-H ₂ O Mixtures	28
9. Removal of Chloride From Green N_2O_4	32
10. Analytical Methods and Results for H ₂ O Equivalent in N_2O_4	33
11. Residue Analysis	61

PHASE I: LABORATORY TESTING

INTRODUCTION

The phenomenon termed "flow decay" has been under investigation at Rocketdyne under both company-funded and AFRPL-sponsored programs since November 1964. The process of flow decay is defined as a spontaneous decrease in the flow-rate through a constant pressure flow system. "Brown" N_2O_4 propellant defined by MIL-P-26539A and MIL-P-26539B was found to be susceptible to the flow decay phenomenon. The cause of the phenomenon was at first elusive but subsequently was shown by both physical and chemical means to be the result of deposition in valve orifices of crystalline $NOFe(NO_3)_4$ formed by corrosion of iron alloys by the N_2O_4 propellant. Laboratory reproduction of this deposition is now routine (Ref. 1).

The effect of low concentrations, 0.25 weight percent (w/o), of selected additives on the solubility of $NOFe(NO_3)_4$ was also investigated. This study identified four additives, acetonitrile, ethyl acetate, benzonitrile, and perfluorooctonitrile as being effective in dissolving flow decay deposits in a flow system, although there were marked differences in the speed with which the different additives dissolved the deposits.

In this program, the objectives under Phase I, Laboratory Testing were first to examine the four above mentioned candidate additives with respect to their ability to dissolve $NOFe(NO_3)_4$ deposits arising from "green" N_2O_4 containing 0.6 weight percent NO and a use limit of 0.2 weight percent water equivalent. To be determined were the best additive, the effect of additive concentration, and the effective life of the additive- N_2O_4 solution under accelerated aging by elevated temperature storage. Second, the chemistry of the additive- $NOFe(NO_3)_4$ interaction was to be examined by both synthetic and analytical techniques and correlated with results obtained for removal of deposits in the laboratory flow system. Third, the effect of NOCl content on corrosion of iron in N_2O_4 propellant was to be investigated by comparison with chloride-free propellant.

About midway through the contract period, it was found that changes in deposition techniques (particularly the temperature of the propellant during recycle) resulted in a change in the physical and chemical nature of the iron-containing deposits. Viscous liquid deposits were obtained which failed to dissolve in the additive-containing solutions previously found to be effective for dissolution of crystalline $\text{NOFe}(\text{NO}_3)_4$ deposits. Accordingly, work on the original four additives was left incomplete and the objectives of Phase I were modified.

The new objectives were first to examine four new candidate additives with respect to their ability to dissolve the viscous liquid deposits in green N_2O_4 (0.6 percent NO , 0.2 percent H_2O equivalent).

The new additives which were chosen on the basis of being stronger complexing agents for iron and being soluble and stable in N_2O_4 were hydrogen fluoride, phosphorus trifluoride, picric acid, nitroform, and dimethyl sulfoxide. Nitroform was later excluded for reasons of safety. Again the best additive, the effect of additive concentration, and the effective life were to be determined.

Second, an investigation of the formation of the viscous liquid deposit from solid $\text{NOFe}(\text{NO}_3)_4$ in green N_2O_4 was to be undertaken. Four variables were studied; water equivalent concentration, $\text{NOFe}(\text{NO}_3)_4$ level, temperature and time.

EXPERIMENTAL SYSTEM

Laboratory Depositor

The laboratory depositor was a modification of that previously used (Ref. 1) and is depicted schematically in Fig. 1. The system consisted of two pairs of 1-liter stainless-steel tanks wrapped with heating tapes and equipped with 0 to 100-psi pressure gages. Each pair of tanks, a

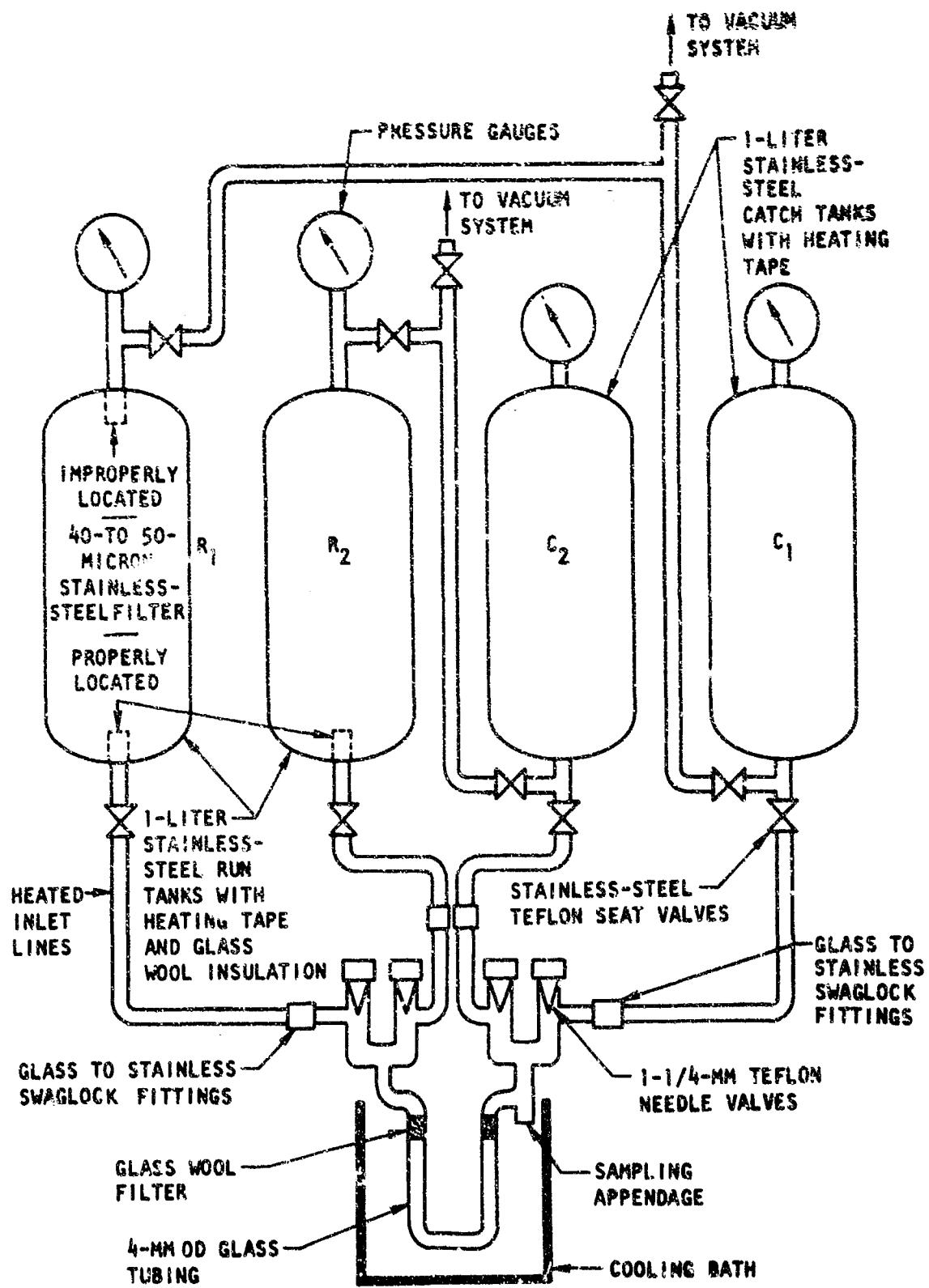


Figure 1. Laboratory Depositor Schematic

run tank (B) and a catch tank (C), was connected in parallel through a common glass U-trap. Each of the run tanks was fitted with a 40-55 micron, cylindrical stainless-steel filter welded to the tank outlet bushing. Recycle lines led from the bottom of the catch tanks to the top of the respective run tanks.

The 4-millimeter OD glass U-trap was replaced by a 0.25-inch Teflon bellows trap with heat shrinkable Teflon-to-metal seals for experiments involving both HF and PF₃ solutions. Both trap systems were tested pneumatically at 100 psig before use with N₂O₄.

RESULTS AND DISCUSSION

Deposition of Solid Flow Decay Material

Deposition of NOFe(NO₃)₄ from N₂O₄ had been demonstrated previously in the laboratory depositor (Ref. 1), but the best conditions found were heating the propellant for 3 days at 130 to 140 F (55 to 60 C) in a stainless-steel cylinder followed by passing the liquid through an ice-cooled glass tube at roughly 15 ml/min. Clearly, a less time consuming, higher yield procedure was required to produce deposits to study the effectiveness of additives either for dissolution of these deposits or for prevention of deposition. Because it appeared that deposition of NOFe(NO₃)₄ from the N₂O₄ was a simple crystallization from a saturated solution, resulting from a temperature differential between the bulk propellant and the deposition site, synthetically prepared NOFe(NO₃)₄ was selected as the "soluble iron" source for the current program. An important, though not initially recognized, difference between the previous work (Ref. 1) and the present program was the change in the propellant from dry brown N₂O₄ of 0.1 percent H₂O equivalent to wet green N₂O₄ of 0.2 percent H₂O equivalent.

A 3.84-gram quantity of synthetically prepared $\text{NOFe}(\text{NO}_3)_4$ (Ref. 1) was used without purification to saturate a 770-milliliter quantity of N_2O_4 (0.9 w/e NO and 0.2 w/e H_2O equivalent). The solid material responsible for the flow decay and previously identified as $\text{NOFe}(\text{NO}_3)_4$ was deposited from this solution in the glass U-trap where the ability of additive N_2O_4 solutions to dissolve it subsequently could be visually observed. All runs which produced a good deposit of $\text{NOFe}(\text{NO}_3)_4$ were made with the solid $\text{NOFe}(\text{NO}_3)_4$ unknowingly retained in the ullage in the improperly located filter (see Fig. 1). The experimental conditions used in each of the $\text{NOFe}(\text{NO}_3)_4$ deposition runs are summarized in Table I.

The procedure for a typical, successful run was as follows. The N_2O_4 contained in the insulated tank B_1 was heated to pressurize it to approximately 100 psig, and the temperature of the inlet line to the glass U-trap was maintained slightly above that of the run tank to prevent deposition in the inlet. During a run, all valves between tanks B_1 and C_1 were wide open with the exception of the Teflon needle valve on the U-trap outlet. Although some of the $\text{NOFe}(\text{NO}_3)_4$ deposited along the walls of the ice-cooled U-trap, most of the solid was collected on the outlet glass wool filter.

Although unknown at the time, the solid $\text{NOFe}(\text{NO}_3)_4$ thought to be saturating the propellant was retained in the ullage space by the improperly located filter (see Fig. 1). All transfers of the heated N_2O_4 were made under autogenous pressure. During the recycle of propellant through the $\text{NOFe}(\text{NO}_3)_4$ in the filter to the run tank B_1 , which was cooled, sufficient solid dissolved to form a good deposit in the subsequent run. After five successful deposition runs, the catch tank C_1 was no longer heated during the recycle process and subsequent deposits became smaller and more difficult to observe. Disassembly of run tank B_1 revealed the mechanical cause of the trouble and the filter was properly located at the tank outlet. This mechanical error, although costly in time, proved to be serendipitous in that it helped to clarify the relationship of the solid and liquid flow decay deposits (vide infra).

TABLE 1

EXPOSITION OF NOFE₄(NO₃)₄

Run No.	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Approximate Catch Tank Recycle Temperature, F	Remarks
1	70 to 86	77	18	(a, b)	No deposit
2	100 to 105	158	45	120 to 140	Normal deposit
3	100 to 105	158	40	120 to 140	Normal deposit
4	108	165	44	120 to 140	Normal deposit
5	108	165	45	90 to 100	Normal deposit
6	100 to 105	167	45	70 to 90	Small deposit
7	108	163	42	70 to 90	Small deposit plus trace liquid
8	100 to 110	163 to 167	33	70 to 90	Small deposit
9	104 to 105	163	34	70 to 90	Very small deposit
10	95 to 105	149	11	70 to 90	Trace deposit from ca. 1/4 of N ₂ O ₄ solution remaining after analysis
	100 to 105	162 to 172	11		
	100 to 105	158 to 169	11		
	100 to 110	158 to 167	12		
11	103	158 to 167	33	(a, c)	Normal deposit plus trace liquid
12	100 to 102	171	30	(a, d)	Small deposit
13	70 to 76	158	23	70 to 90	Heated at 175 F for 1.5 hours just prior to run through Teflon trap. No deposit formed; no flow decay in throttling valve.

(a) Run tank filled with fresh N₂O₄

(b) NOFE₄(NO₃)₄ in ullage in runs 1 through 10

(c) Same solid NOFE₄(NO₃)₄ as used in runs 1 through 10 in contact with liquid N₂O₄

(d) No NOFE₄(NO₃)₄ added to propellant

Before it was determined that the difference in the quantity of the $\text{NOFe}(\text{NO}_3)_4$ deposit in the first runs (1 through 6) and those immediately following (7 through 10) was due to the combination of the lower recycle temperature and the improperly located filter, an analysis of the N_2O_4 solution was undertaken. After removal of an estimated 10 to 12 millimoles of CO (identified by vapor pressure measurements, 400 millimeters at -196°C), the residual vapor above the N_2O_4 solution was shown by mass spectroscopy to contain 1.1-percent CO_2 . The CO and CO_2 presumably arise from incompletely reacted $\text{Fe}(\text{CO})_5$, which had been used to prepare the crude $\text{NOFe}(\text{NO}_3)_4$. The analytical data obtained on the N_2O_4 solution, when compared with the data obtained before contacting it with $\text{NOFe}(\text{NO}_3)_4$, showed nothing which could account for the observed behavior (Table 2). Noteworthy, however, is that a high value was obtained for water equivalent based on the observed NO value (cf. Table 10, page 33).

TABLE 2
ANALYSIS OF PROPELLANT

	Found As Received	Calculated After H_2O Addition	Found After $\text{NOFe}(\text{NO}_3)_4$ Treatment
w/o N_2O_4	99.36	98.88	98.97
w/o NO	0.63	0.91	0.78
w/o H_2O equiv	0.03	0.20	0.15*
w/o NOCl	0.01	0.01	0.01
ppm Fe	—	—	1.4

*Calculated to be 0.12 to account for moles of NO present

Deposition of Liquid Flow Decay Material

The same solid iron compound used to deposit $\text{NOFe}(\text{NO}_3)_4$ was transferred from the filter into the tank R_1 which was recharged with fresh green N_2O_4 of 0.2 % H_2O equivalent. The first run in the reassembled depositor, with the filter now properly located, produced a normal deposit of $\text{NOFe}(\text{NO}_3)_4$, but in subsequent runs the deposit consisted of a mixture of a dark brown viscous liquid and a light beige solid chemically unlike the initial $\text{NOFe}(\text{NO}_3)_4$. The liquid appeared to be the same as that described by TW (Ref. 2).

The experimental procedure for deposition of liquid was the same as had been used previously for formation of solid $\text{NOFe}(\text{NO}_3)_4$ deposits. The temperature of the catch tank C_1 was 70 to 90 F in all experiments.

Experimental conditions used in each run are summarized in Table 3. The liquid-solid mixture (Fig. 2) from runs 14 through 17, collected in an appendage downstream of the glass wool outlet filter (see Fig. 1), was used for analysis. The 0.00800-gram liquid sample analyzed 16.6-percent Fe, 68.6-percent NO_3^- , and 26.3-percent NO_2^- (equivalent to 17.1-percent NO_+) and the 0.01654-gram solid sample with admixed liquid analyzed 17.7-percent Fe, 62.9-percent NO_3^- , and 6.8-percent NO_2^- (equivalent to 4.5-percent NO_+).

From the foregoing analyses, ratios of $\text{Fe}/\text{NO}_3^-/\text{NO}_2^-$ were for the liquid 1/3.72/1.92 (102 percent material balance) and for the solid-liquid mixture 1/3.21/0.47 (85 percent material balance). These data do not lead directly to rational empirical formulae, but speculative compositions may be suggested such as an equimolar mixture of $\text{NOFe}(\text{NO}_3)_4$ and HNO_2 for the liquid (ratio 1/4/2) and $\text{Fe}(\text{H}_2\text{O})_6^{+++}\text{Fe}(\text{NO}_3)_4^- (\text{NO}_3)_2^-$ for the solid (ratio 1/3.25/0.50 for 3:1 mixture of solid and liquid). X-ray diffraction powder data (Table 4) showed that the deposited solid was not $\text{NOFe}(\text{NO}_3)_4$.

TABLE 3

DEPOSITION OF LIQUID FLOW DECAY MATERIAL

Run No.	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Remarks
14	103 ^(a)	149 to 167	33	Liquid plus solid
15	115 to 120	167 to 171	36	Liquid plus solid
16	110	167 to 171	36	Very little deposit
17	115 to 120	167 to 171	46	Liquid plus solid
18	95 to 100	151 to 160	55	Small liquid deposit
19	94 to 101	165 to 169	70	Small liquid deposit
20	96 to 100	163 to 165	72	Small liquid deposit
21	96 to 100	156 to 160	45	Small liquid deposit
22	100 to 105	154 to 160	30	Small liquid deposit
23	100 to 110	156 to 160	20	Small liquid deposit
24	102 to 110	160 to 163	27	Small liquid deposit
25	105 to 108	167 to 171	36	Liquid plus solid
26	102 to 106	158 to 165	31	Small liquid deposit
27	105 to 110 ^(b)	154 to 167	36	Liquid deposit
28	110 to 115 ^(c)	165 to 169	42	Liquid deposit
29	110 to 115 ^(c)	160 to 167	43	Liquid deposit
30	110 to 115 ^(b)	156 to 169	45	Liquid deposit
31	105 to 115 ^(c)	163 to 169	42	Liquid deposit
32	110 to 115 ^(c)	163 to 169	42	Liquid deposit
33	96 to 100	149 to 160	51	Liquid deposit
34	115	171	46	Liquid deposit
35	115	154 to 163	44	Liquid deposit
36	115	149 to 163	34	Liquid deposit
37	115	163 to 171	39	Liquid deposit
38	112 to 115	156 to 169	36	Liquid deposit

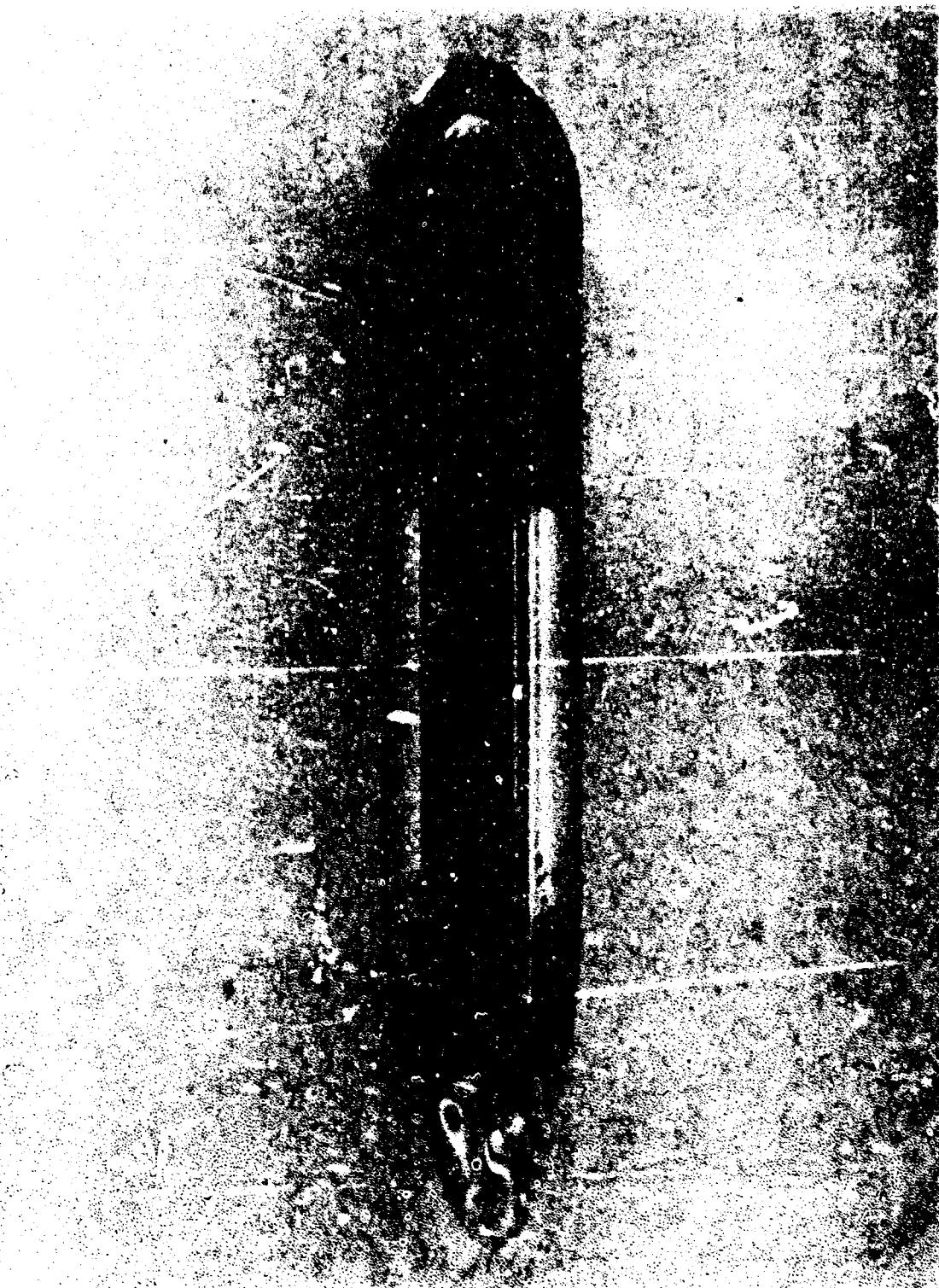
TABLE 3
(Concluded)

Run No.	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Remarks
39	112 to 115	156 to 162	33	Liquid deposit
40	115	163 to 169	42	Liquid deposit
41	115	156 to 169	50	Liquid deposit
42	110 to 115	158 to 165	44	Liquid deposit
43	112 to 115	153 to 163	38	Liquid deposit
44	110 to 115	163	45	Liquid deposit

(a) Inadvertently heated to an estimated 175 F just before run
 (b) Held at temperature for 16 hours before run
 (c) Held at temperature for 1.5 hours before run

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Figure 2. Liquid-Solid Mixture Flow Decay Deposit



A 0.01440-gram sample of the residual yellow solid recovered after run 11 from the run tank R₁ analyzed 25.3-percent Fe, 62.1-percent NO₃⁻, and 0.1-percent NO₂⁻. This gives a Fe/NO₃⁻ ratio 1/2.16 with NO₂⁻ absent, suggesting an oxynitrate such as FeO(NO₃)₂·H₂O_x. The X-ray powder diffraction data for this residual solid are contrasted with those data for the original NOFe(NO₃)₄ in Table 4.

Duplication of the deposition of a liquid-solid mixture was achieved using the same quantities of fresh NOFe(NO₃)₄ and N₂O₄ as were used initially in the NOFe(NO₃)₄ deposition. Thus, contact time, as well as water equivalent concentration, was indicated to be an important variable bearing on the physical and chemical nature of the iron-containing deposits.

Additive Effectiveness and Life

A number of Lewis bases had been shown previously (Ref. 1) to be effective additives both for preventing deposition and for dissolving deposits of NOFe(NO₃)₄. In all of these earlier studies, a single additive concentration of 0.25 w/o was used and the studies of the effective life of the additives were rudimentary and incomplete. Accordingly, each of the additives in this program was to be studied at three concentrations, 0.25, 0.10, and 0.05 w/o, and tested periodically until they failed to dissolve NOFe(NO₃)₄ under accelerated aging at 150 to 155 F. The four candidate additives were acetonitrile, ethyl acetate, benzonitrile, and perfluoroacetonitrile.

When it was found that the wet, green N₂O₄ gave liquid deposits (rather than solid NOFe(NO₃)₄) that did not dissolve in the additive solutions under investigation, the study was restricted to 0.25 w/o additive solutions except for acetonitrile. Another series of four additives, hydrogen fluoride, phosphorus trifluoride, picric acid, and dimethylsulfoxide, was selected for investigation at 0.25 w/o concentration to

TABLE 4

CuK_α X-RAY DIFFRACTION POWDER DATA OF NOFe(NO₃)₄ BEFORE
AND AFTER EXPOSURE TO GREEN N₂O₄ (0.2 w/o H₂O EQUIVALENT)

NOFe(NO ₃) ₄ [*]	d-spacing, Å (intensity)		Solid Codeposited With Liquid From Wet Green N ₂ O ₄
	Residual Yellow Solid After Heating in Wet Green N ₂ O ₄		
6.3 vvs	6.40 s		6.40 v
5.8 vvs	6.00 s		5.80 mw
5.3 s	4.40 vw		5.10 mw
4.20 m	4.05 ms		4.30 ms
3.70 s	3.68 vw		3.71 ms
3.48 s	3.39 v		3.39 ms
3.20 s	3.30 s		3.30 ms
3.10 vs	3.10 z		3.20 ms
3.00 vs	2.79 vw		2.79 ms
2.44 m	2.05 vw		2.51 mw
2.35 v	2.33 v		2.38 v
2.28 m	2.05 v		2.28 v
2.17 v	1.79 vw		2.20 v
1.98 w			2.01 vw
1.88 w			1.88 vw
1.78 w			

*Ref. 1

determine if these materials could dissolve the liquid deposit or prevent its formation. The results for each of the eight additives are discussed separately.

The compositions of additive-containing solutions in wet, green N_2O_4 , prepared to evaluate the effectiveness of these additives in dissolving the deposits, are listed in Table 5. Table 6 summarizes the experimental conditions used in each of the runs testing the effectiveness of each of the additive-containing solutions together with the results observed.

The deposition of a dark brown viscous liquid from the acetonitrile solutions (runs 48, 50, 53, and 54, Table 6) prompted a detailed analysis of the 0.24 w/o solution (A-1, Table 5) to determine what changes in composition had occurred as a result of heating for 14 days at 150 to 155 F. Found (in weight percent): N_2O_4 , 98.70; NO, 0.85; NOCl, 0.01; H_2O equiv, 0.01; Fe, 0.00104 (10.4 ppm). Mass spectrometric analysis of both liquid and vapor phases of solution A-1 showed N_2 (from air), 2.8 percent (in the liquid) and 3.1 percent (in the vapor); CO_2 , 0.7 percent (in the liquid and 1.1 percent (in the vapor); CH_3CN , absent (both liquid and vapor).

The solubility of the liquid deposit (from F-3, Table 7) in 0.25 w/o DMSO- N_2O_4 was studied in a static system by decanting the N_2O_4 phase from the viscous brown liquid and replacing it with 38 milliliters of the DMSO solution (H-1, Table 5). No change was apparent in the viscous liquid, but on standing several days colorless crystals were observed in the N_2O_4 phase.

TABLE 5
COMPOSITIONS OF ADDITIVE-N₂O₄ SOLUTIONS

Solution No.	Additive	Additive Weight grams	Water, grams	N ₂ O ₄ , (a)	Weight Percent		
					Additive	N ₂ O ₄	NO
A-1	CH ₃ CN	2.7057	1.8834	1108.4	0.24	98.67	0.91
A-2	CH ₃ CN	1.1655	1.8559	1110.6	.10	98.81	0.91
A-3	CH ₃ CN	0.5646	1.8312	1110.3	0.05	98.88	0.90
B	CH ₃ COOC ₂ H ₅	2.7861	1.8645	1107.1	0.25	98.66	0.91
C	C ₆ H ₅ CN	2.8198	1.7855	1103.6	0.25	98.67	0.90
D	CF ₃ CN	2.786 (b)	1.6525	1114.1	0.25	98.73	0.87
E-1	HF	3.4593	1.7360	1103.1	0.31	98.63	0.89
E-2	HF	3.8653	1.7046	1108.6	0.35	98.61	0.88
F	(NC ₂) ₃ C ₆ H ₂ OH	2.8314	1.7300	1117.2	0.25	98.70	0.88
G	PF ₃	2.83 (b)	1.7499	1110.9	0.25	98.69	0.89
H-1	(CH ₃) ₂ SO	0.1043	0.0725	40.7704	0.25	98.62	0.92
H-2	(CH ₃) ₂ SO	2.7637	1.8284	1111.6	0.25	98.68	0.90

(a) Analysis: 99.36 w/o N₂O₄, 0.63 w/o NO, 0.03 w/o H₂O equivalent, and 0.01 w/o NaCl
(ignored because value was subsequently shown to be 0.0013 w/o).

(b) Calculated weight based on STP volume of gas measured.

TABLE 6

ADDITIVE EFFECTIVENESS AND LIFE

Run No.	Solution No. (see Table 4)	Deposit Run No.*	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Remarks
45	A-1	1 to 2	100 to 105	172	27	Deposit dissolved
46	A-1	4	102	163 to 167	22	A-1 stored 7 days at 150 to 155 F. Deposit dissolved in 1 to 2 minutes.
47	A-1	12	95 to 105	176	20	A-1 stored 14 days at 150 to 155 F. Deposit appeared not to dissolve.
48	A-1	9	100 to 102	165 to 167	26	A-1 stored 14 days at 150 to 155 F. Deposit appeared to dissolve but change was very difficult to discern. A significant amount of dark viscous liquid deposited.
49	A-1	9 (rerun)	100 to 105	158 to 172	46	No cooling on U-trap. No change in amount of viscous liquid.
50	A-1	None	98 to 103 110 to 115 110	163 to 167 163 165	24 15 18	Only in first pass did viscous liquid collect
51	A-2	3	100 to 105	158 to 163	88	Particulate matter plugging inlet glass wool filter due to emission of filter in R ₂ .
52	A-2	5	162 to 104	163 to 169	28	Deposit dissolved in 1 to 2 minutes.
53	A-2	12 (rerun)	105 to 110	172	39	A-2 stored 7 days at 150 to 155 F. Deposit appeared not to dissolve and liquid also deposited.

*From Table 1 or 3

TABLE 6
(Continued)

Run No.	Solution No. (see Table 4)	Deposit No.* Run No.*	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Remarks
54	A-2	7	100	165 to 172	35	A-2 stored 7 days at 150 to 155 F. deposit appeared to dissolve but change was very difficult to dis- cern. A viscous brown liquid phase was deposited.
55	A-3	6	100 to 102	167	27	Deposit dissolved in 1 to 2 minutes.
56	A-3	8	96 to 102	180	25	A-3 stored 7 days at 150 to 155 F. Deposit appeared to dissolve but change was difficult to discern due to small size and presence of residual liquid deposit from run 54.
57	B	11	102 to 110	180 to 181	19	Deposit dissolved in 2 to 3 minutes.
58	C	14 to 17 (residual)	105 to 110	167	20	Partial dissolution of liquid deposit.
59	C	14 to 17 (residual- rerun)	105 to 110	167	26	No further dissolution of liquid deposit
60	D	33	103 to 105	156 to 160	36	Liquid deposit did not dissolve.
61	E-1	18	94 to 100	160	91	Run incomplete due to plugging from HF attack on glass. Liquid deposit appeared unaffected.
62	E-2	22 to 32	16 to 20	77	40	Run in Teflon trap. No visible effect on liquid deposit but it crystallized on pumping off N_2O_4 .
63	E-2	None	36 to 46	77	7	0.050-gram $MnFe(NO_3)_4$ added to E-2. No deposit formed in Teflon trap.

*From Table 1 or 3

TABLE 6
(Concluded)

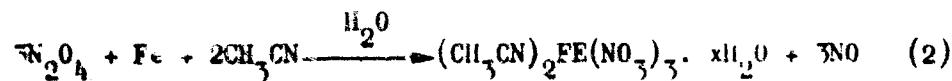
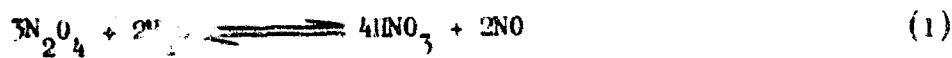
Run No.	Solution No. (see Table 4)	Deposit No. Run No.*	Run Tank Pressure, psig	Inlet Line Temperature, F	Run Time (770 ml), minutes	Remarks
64	E-2	None	72 to 80	77	42	0.050-gram NOFe(NO ₃) ₂ added to E-2. No deposit formed in Teflon trap but flow decay observed in throttling valve (cf., blank run 13, Table 1).
65	F	22 to 32 (residual)	105 to 110	154 to 162	35	Partial crystallization of liquid deposit.
66	F	22 to 32 (residual- rerun)	110 to 115	160 to 162	37	Liquid portion dissolved when U-trap was not cooled.
67	G	34 to 41	60 to 70	77	22	No visible effect on liquid deposit.
68	G	34 to 41 (rerun)	69 to 73	77	17	No visible effect on liquid deposit.
69	H-2	42	112 to 117	160 to 162	32	Liquid deposit dissolved.
70	H-2	43	114	158	0.25	Liquid deposit dissolved in 15 seconds—run terminated.
71	H-2	44	112 to 115	163	36	H-2 stored 17 days at 150 F. Liquid deposit dissolved in 30 seconds.

*From Table 1 or 3

Acetonitrile. Acetonitrile solutions at 0.24, 0.10, and 0.05 w/o in green N_2O_4 were equally effective in dissolving deposits of $NOFe(NO_3)_4$. The fresh solutions were heated in tank R_2 (Fig. 1) to develop a driving pressure of 100 to 105 psig and passed to catch tank C_2 through the glass U-trap containing the brown solid deposit at flowrates of 27 to 28 ml/min. The $NOFe(NO_3)_4$ was solubilized in the first 1 to 2 minutes of the 27 to 28 minute runs. The 0.24 w/o acetonitrile solution remained effective after 7 days storage at 150 to 155 F; after 14 days it appeared by visual observation no longer to be effective. However, this test was made on a very small deposit and consequently the result is somewhat uncertain. The same uncertainty is to be noted in the apparent loss of effectiveness of the 0.10 and 0.05 w/o acetonitrile solutions after heating for 7 days at 150 to 155 F.

Each of the acetonitrile solutions, after the period of accelerated aging, deposited a second liquid phase when passed through the ice-cooled glass U-trap. The most concentrated solution gave the largest droplet of the dark brown viscous liquid, which was shown to be slightly soluble in N_2O_4 (no deposit without cooling) and water soluble. However, the quantity was too small for further direct characterization. The analysis of the propellant (described below) gave indirect evidence for the composition of this liquid deposit.

Mass spectrometric analysis of the 0.24 w/o acetonitrile solution (A-1, Table 5) indicated the complete absence of acetonitrile in both the liquid and the vapor phases, with CO_2 and N_2 as the major impurities in the vapor. Comparison of the analysis of A-1 with its calculated composition (Table 5) suggests that corrosion of the stainless-steel tank must have occurred. The dramatic decrease in H_2O equivalent (from 0.20 to 0.01 w/o) would require a corresponding decrease in NO concentration (from 0.91 to 0.59 w/o) according to Eq. 1.



Corrosion of the cylinder (approximately 0.0002 inch), presumably enhanced by the acetonitrile (Eq. 2), could supply the necessary NO to bring the concentration to the observed 0.85 w/o. The amount of CH_3CN required (Eq. 2) correlates well with that actually used: 64 μ moles (required), 65.8 μ moles (in A-1). The concentration of iron in the N_2O_4 -acetonitrile solution after heating was found to be almost an order of magnitude greater (10.4 ppm) than in N_2O_4 alone (Ref. 1).

Although the direct study of the stoichiometry of the reaction of acetonitrile with $NOFe(NO_3)_4$ was deleted when the program objectives were changed, the ratio of 2:1 was obtained indirectly from these analytical data. Also inferred is an enhanced corrosivity for the additive-containing solution as long as free acetonitrile remains (Ref. 4 reports this system nonreactive, however). Because acetonitrile appears to dissolve $NOFe(NO_3)_4$, only to substitute another slightly soluble iron-containing compound for it, this additive offers no solution to the problem of decreasing flowrates in N_2O_4 systems caused by deposition of corrosion products.

Ethyl Acetate. A solution 0.25 w/o ethyl acetate effectively removed a deposit of $NOFe(NO_3)_4$ in ca. 2 to 3 minutes when passed through the U-trap at 40 ml/min. This additive appears to require a longer time to dissolve the solid $NOFe(NO_3)_4$ deposit when compared with acetonitrile. This experiment was not definitive, however, because of the presence of a trace of liquid codeposited with the solid. This liquid may be indicative of partial hydration of the iron compound which could change its solubility or rate of solution in the additive solution. Further evaluation of the ethyl acetate solution after 7 days storage at

150 to 155 F was suspended because further attempts to deposit solid $\text{NOFe}(\text{NO}_3)_4$ produced liquid deposits instead, and ethyl acetate was ineffective in dissolution of the liquid deposit.

Benzonitrile and Trifluoroacetonitrile. Solutions of 0.26 w/o benzonitrile and 0.25 w/o trifluoroacetonitrile (both of which solubilize $\text{NOFe}(\text{NO}_3)_4$ (Ref. 1) in N_2O_4 were found to be ineffective in dissolution of the viscous liquid deposit. No further evaluation of these additives was attempted.

Hydrogen Fluoride. A preliminary run was made in the glass U-trap on the assumption that any gross effects that 0.31 w/o HF in N_2O_4 might exhibit on contacting a liquid deposit would not be obscured by the HF-glass interaction. The HF appeared not to have any effect on the liquid deposit, but the pattern of glass etching which resulted left considerable doubt as to the HF concentration in the vicinity of the liquid deposit. Accordingly, the glass U-trap and glass wool filter plugs were replaced by a Teflon U-trap with carbon felt filter plugs. The experiment was repeated using a liquid deposit which had been mechanically introduced into the Teflon U-trap. No visual change in the dark viscous liquid was noted during the run, but on subsequent evacuation of the trap the liquid became colorless and then crystallized, suggesting perhaps formation of NOFeF_4 (cf. NO_2FeF_4 , Ref. 1). HF appears unsuitable as an additive for dissolution of liquid flow decay deposits.

A series of three runs was made in the Teflon U-trap to determine whether 0.35 w/o HF would prevent deposition of any iron-containing material (liquid or solid) from N_2O_4 containing $\text{NOFe}(\text{NO}_3)_4$ in 2 to 4 times excess of the ambient temperature solubility. No deposition was observed in any of these runs, each of which was made under conditions less drastic than the usual deposition run. A deposition run, made as a control under these more mild conditions, using the N_2O_4 saturated with a large excess of $\text{NOFe}(\text{NO}_3)_4$, also was unsuccessful. The liquid deposit apparently either fails to form under the less drastic conditions or fails to adhere to the Teflon or carbon surfaces the way it does to glass.

Picric Acid. Contact of a 0.25 w/o picric acid- N_2O_4 solution with the liquid deposit in the ice-cooled U-trap resulted in partial crystallization of the liquid droplets. A second run without cooling produced no further change in the crystalline solid, but the liquid portion of the deposit was soluble in the hot (150 F) picric acid- N_2O_4 solution. During storage at ca. 150 to 155 F, the pressure over the 0.25 w/o picric acid- N_2O_4 solution increased slowly over 80 days, amounting to an increase at ambient temperature of about 15 psi. This oxidative instability plus conversion of the liquid deposit to an insoluble solid eliminated picric acid from further consideration as an effective additive.

Phosphorus Trifluoride. A 0.25 w/o $PF_3-N_2O_4$ solution was tested twice by passing it over liquid deposit which had been mechanically introduced into a Teflon U-trap. No further evaluation was attempted after no visual change in the dark viscous liquid could be detected.

Dimethylsulfoxide. In a preliminary experiment, a 0.25 w/o dimethylsulfoxide- N_2O_4 solution (H-1) was stored at 150 to 155 F for 13 days. When the solution was subsequently cooled to ambient temperature, no pressure increase was observed demonstrating the stability of the additive in N_2O_4 .

Another 0.25 w/o dimethylsulfoxide- N_2O_4 solution (H-2) was passed over a liquid deposit and was observed near the middle of the run to have dissolved the deposit. A confirmatory run was terminated abruptly when the deposit disappeared completely in the first 15 seconds and the mixture was placed in an oven to accelerate aging of the solution. The additive-containing solution, after storage at 150 F for 17 days, was passed over another liquid deposit and found to dissolve it in 30 seconds indicating that DMSO was an effective additive for dissolving liquid flow decay deposits.

An attempt to confirm the solubility of the liquid deposit was made using 0.25-percent DMSO- N_2O_4 (0.25 w/o H_2O equivalent) solution and the liquid deposit formed from $NOFe(NO_3)_4$ and wet N_2O_4 (experiment F-3, Table 6, 0.503 w/o water equivalent). In this case the liquid appeared not to dissolve, but after several days at ambient temperature, colorless crystals deposited from the N_2O_4 phase. These observations tend to substantiate the postulated formation of two liquid deposits of different chemical composition which is dependent on the water equivalent concentration of the N_2O_4 , and only the first of which is soluble in the DMSO solution. Further evidence for the existence of two visually indistinguishable but chemically different liquid deposits is set forth in the next section.

Effect of Water-Equivalent Concentration on $NOFe(NO_3)_4$

Previous investigations of the flow decay phenomenon at Rocketdyne using brown N_2O_4 of 0.1 w/o H_2O equivalent indicated that observed decreases in flowrate were caused by the deposition of crystalline $NOFe(NO_3)_4$ (Ref. 1). Other laboratories using green N_2O_4 (0.6 w/o NO , 0.1 w/o H_2O equivalent) reported clogging in dynamic systems caused by a viscous dark liquid containing both zinc and iron (Ref. 2). Each of these metals had been introduced into the propellant as the crude product formed by reaction of the metal chloride with N_2O_4 in the presence of ethyl acetate, and thus could have been solvated; e.g., $(CH_3COOC_2H_5)_2NOFe(NO_3)_4$ or $(CH_3COOC_2H_5)_2Fe(NO_3)_3 \cdot xH_2O$.

In the deposition experiments reported herein, green N_2O_4 of higher water equivalent concentration (i.e., 0.2 w/o) was found to deposit either a crystalline solid having the same chemical behavior as $NOFe(NO_3)_4$ toward Lewis base-type additives or a dark viscous liquid. At this particular H_2O equivalent concentration, the type of deposit appeared to depend on

the contact time between the propellant and the $\text{NOFe}(\text{NO}_3)_4$ used to saturate the solution. After contact times longer than a few hours, the iron-containing material which deposited from the solution was a dark viscous liquid sometimes accompanied by a crystalline solid differing in both physical and chemical properties from $\text{NOFe}(\text{NO}_3)_4$. Therefore, in addition to the effects of contact time and H_2O equivalent concentration, on $\text{NOFe}(\text{NO}_3)_4$, the effects of temperature and iron level were included in the study of the parameters responsible for the properties of the iron-containing deposits.

The effect of water equivalent concentration on the physical state of $\text{NOFe}(\text{NO}_3)_4$ and the degree of hydration of $\text{NOFe}(\text{NO}_3)_4$ which causes these changes of state was studied in a series of experiments at five water equivalent concentrations, two iron levels, and two temperatures. Weighed amounts of $\text{NOFe}(\text{NO}_3)_4$ were placed in 10-milliliter, heavy-wall tubes closed to Teflon needle valves. Approximately 7 milliliters (10 grams) of green N_2O_4 (0.58 w/o NO) of varying known water equivalent concentration was weighed into each tube. The tubes were immersed in constant constant temperature oil baths for 168 hours during which time changes in the physical appearance of the mixtures were noted. At the conclusion of the heating period, the tubes were cooled to ambient temperature and immediately thereafter the N_2O_4 phases were sampled for ^1H nmr analysis in precision nmr tubes. Further changes in the appearance of the mixtures at ambient temperature were noted. The experimental data and observed changes are listed in Table 7.

The N_2O_4 solutions of varying water equivalent concentration were prepared in glass by mixing weighed amounts of two stock solutions, one dry and one wet, the preparation of which are described as follows. The dry stock solution was prepared in glass by stirring approximately 1 liter of green N_2O_4 (0.59 w/o NO , 0.03 w/o H_2O equivalent) with 10-grams P_2O_5 at ambient temperature. The mixture was allowed to stand overnight and subsequently distilled at ambient temperature into an ice-cooled receiver. The wet stock solution was prepared in glass by

TABLE 7

INTERACTION OF $\text{NOFe}(\text{NC}_3)_4$ WITH GREEN N_2O_4 OF VARIOUS
WATER EQUIVALENT CONCENTRATIONS

Run No.	Water Equivalent Concentration, wt. %	Green N_2O_4 , wt. %	Initial N_2O_4 Residue, wt. %	After 100 Hours, wt. %	Temperature, $^{\circ}\text{C}$	H_2O , ml.	From H_2O moles	Molar Ratio of H_2O Residues/%	Observed Change of $\text{NOFe}(\text{NC}_3)_4$	
									After 100 Hours	After 100 Hours
B-3	5.13	0.1572	10.1263	10.2493	9.453	100.0	0.283	2.69	2 hours; partial liquification and crystallization, 57 hours; crystalline solid (no change at ambient)	
B-4	11.39	0.1046	10.2470	10.2470	11.250	117.8	0.250	2.50	1.5 hours; partial liquification and crystallization, 58 hours; crystalline solid (liquified at ambient)	
C-1	5.1	0.0160	10.1114	10.1114	9.446	100.0	0.333	20.81	2 hours; solid liquified (a few crystals formed at ambient)	
P-2	6.96	0.0142	10.1292	10.1292	9.446	117.8	0.322	17.69	2 minutes; solid liquified 2 hours; started to crystallize, 70 hours; crystalline solid (a few crystals remain at liquid at ambient)	
P-3	12.52	0.13867	10.1165	10.1165	11.250	114.0	0.294	6.61	68 hours; solid liquified (no change at ambient)	
P-4	12.52	0.13867	10.1165	10.1165	11.250	117.4	0.328	4.95	52 hours; solid liquified (no change at ambient)	
P-5	12.52	0.13867	10.1165	10.1165	11.250	Ambient	---	---	17 hours; powder sticky, 2 to 3 days; loosely agglomerated powder became free flowing on shaking	
P-6	12.52	0.13867	10.1165	10.1165	11.250	Ambient	---	---	17 hours; solid liquified	
P-7	12.52	0.13867	10.1165	10.1165	11.250	Ambient	---	---	17 hours; partial liquification and crystallization	
P-8	12.52	0.13867	10.1165	10.1165	11.250	Ambient	---	---	17 hours; complete crystallization	

(a) Residue for 76 hours

(b) Liquified

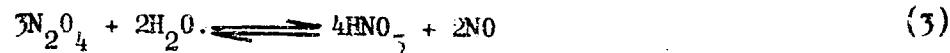
(c) After 100 hours contact

TABLE 7
(Continued)

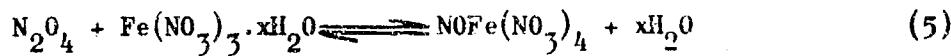
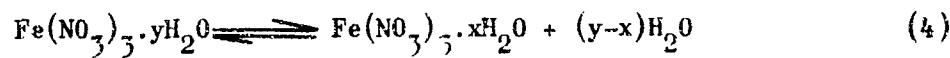
Sample No.	Mol% (NO_3) ₄ wt. mg	Green H_2O wt. g	Initial Mol% H_2O equiv	Mol% H_2O equiv After 150 hours	Temperature, °C	$\frac{\text{H}_2\text{O}_{\text{Resid}}}{\text{H}_2\text{O}_{\text{Initial}}}$	Mol Ratio of $\text{H}_2\text{O}_{\text{Resid}}/\text{H}_2\text{O}_{\text{Initial}}$	Observed Changes of $\text{H}_2\text{O}(\text{NO}_3)_4$	
								Time (hr)	Time (hr)
A-1	7.93	0.00217	10.1946	0.017	7.152 (a)	104.0	-0.006	-1.29	7.6 hours; powder free flowing (no change at ambient)
A-2	4.51	0.0135	10.0824	0.017	0.017 (a)	157.0	0.000	0	7.6 hours; powder free flowing (no change at ambient)
B-1	4.74	0.0162	10.1510	0.045	0.036	104.0	-2.372	-3.07	1.58 hours; powder free flowing (no change at ambient)
B-2	5.16	0.0155	10.1499	0.045	0.048	157.0	-0.017	-1.10	1.68 hours; powder free flowing (no change at ambient)
B-3	34.05	0.1020	10.1395	0.045	0.045	104.0	0.000	0	1.68 hours; powder free flowing (no change at ambient)
B-4	38.05	0.1192	10.2294	0.045	0.053	157.0	-0.059	-0.74	1.68 hours; powder free flowing (no change at ambient)
C-1	5.36	0.0198	10.1922	0.099	0.115	104.0	-0.090	-3.70	2.5 hours; largely agglomerated powder became free flowing on shaking (no change at ambient)
C-2	5.68	0.0170	10.1160	0.099	0.109	157.0	-0.056	-3.29	2.5 hours; largely agglomerated powder became free flowing on shaking (no change at ambient)
C-3	35.11	0.1052	10.1827	0.099	0.100	104.0	-0.006	-0.06	2.5 hours; loosely agglomerated powder became free flowing on shaking (no change at ambient)
C-4	35.44	0.1061	10.1991	0.099	0.099	157.0	0.000	0	2.5 hours; loosely agglomerated powder became free flowing on shaking (no change at ambient)
D-1	5.24	0.0157	10.2679	0.198	0.195	104.0	-0.017	-1.04	4.5 hours; powder aggregated (liquefied at ambient at ambient)
D-2	5.57	0.0167	10.1914	0.192	0.196	157.0	-0.022	-1.32	5.5 hours; powder aggregated (liquefied at ambient at ambient)
D-3	34.33	0.1085	10.0881	0.124	0.202	104.0	-0.056	-0.55	4 hours; powder wispy. 2.5 hours; powder aggregated (no change at ambient liquefied at ambient)
D-4	34.08	0.1021	10.2912	0.192	0.293	157.0	-0.061	-0.60	4 hours; powder aggregated (partially liquefied at ambient)
E-1	9.02	0.0240	16.1078	0.293	0.289	104.0	0.135	5.63	24 hours; solid liquified. 55 hours; partially crystallized (completely crystallized at ambient)
E-2	10.58	0.0517	10.0044	0.293	0.235	157.0	0.353	10.50	2 hours; partial liquefaction and crystallization. 55 hours; crystalline solid (liquefied at ambient)

oxygenating approximately 1 liter of the same green N_2O_4 followed by similar drying and distillation. A portion of the dry brown N_2O_4 was combined with enough water to cause separation of a second liquid phase. After oxygenation of this two phase mixture a weighed portion of the "water phase" was mixed with a weighed portion of the dry brown N_2O_4 and water was added to raise the water equivalent concentration still higher while generating NO (or HNO_2) as well. The preparative and analytical data for the various N_2O_4 solutions are shown in Table 8 together with the standard solutions used for 1H nmr calibration.

In Table 7 are listed the data and observed changes for a series of preliminary qualitative experiments (G-J) and another series of semi-quantitative experiments (A-F). These are interpreted in terms of two processes involving water in the N_2O_4 propellant system. First, the overall reaction for the hydrolysis of N_2O_4 is a complex equilibrium which may be simply represented by Eq. 3.



In N_2O_4 , the concentration of free water is quite low because of the mass action effect, but it is increased with increase in temperature (Ref. 4). Second, the dehydration of a salt hydrate, represented in Eq. 4 and 5, proceeds to a greater degree with increasing temperature.



The phase separation phenomenon which occurs in the N_2O_4 - H_2O system would be expected to occur in the presence of the iron salts which should dissolve preferentially in the "aqueous" phase.

TABLE 8

PREPARATION AND ANALYSIS OF N_2O_4 -NO-H₂O MIXTURES

N_2O_4 Solution Description	w/o H ₂ O Equiv (¹ H nmr)
Green dry stock solution (D) (see text for preparation) 0.58 w/o NO	0.017 0.017 0.017 0.019
Brown wet stock solution (W) (see text for preparation) 0.59 w/o NO	1.27 1.31
56.2124 g D + 1.3786 g W	0.045
53.6003 g D + 4.0596 g W	0.098 0.100
49.2827 g D + 8.2629 g W	0.192
45.4143 g D + 12.0871 g W	0.293
38.7465 g D + 21.8515 g W	0.503
10.14388 g D + 0.01254 g H ₂ O	0.127 0.125 0.131 0.123 0.129
8.66622 g D + 0.02643 g H ₂ O	0.321 0.321 0.296 0.322 0.329 0.318 0.321
9.73619 g D + 0.05068 g H ₂ O	0.535 0.556 0.579 0.539
9.61245 g D + 0.10057 g H ₂ O	1.010

In the preliminary experiments, an unweighed quantity (estimated to be 3 to 5 milligrams) of $\text{NOFe}(\text{NO}_3)_4$ was placed in an nmr tube with about 2 grams of N_2O_4 , the water equivalent concentration of which was measured by nmr spectroscopy both before and after contact with $\text{NOFe}(\text{NO}_3)_4$. Partial hydration caused agglomeration of the solid (experiment G) followed, at increasing initial water equivalent concentrations, by what has been interpreted as a separation of an acid solution of the "hydrated" salt (experiment H) and crystallization of a higher hydrate from this "aqueous" phase (experiments I and J).

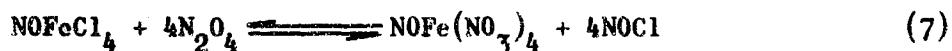
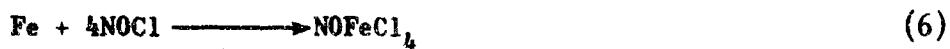
The effects of temperature can be noted qualitatively by comparing pairs of experiments such as D-1 and D-2, E-3 and E-4, etc. In every case, as expected, the changes have occurred more rapidly at the higher temperature. The time required for a given change, such as liquification of the solid, roughly correlates with the initial amount of solid used.

An inspection of the data for experiments A-F indicates that experimental errors (particularly moisture pickup from apparatus and possible weighing errors) have rendered the experiments semiquantitative at best, with those at the higher "iron level" being more self-consistent. The series of experiments (D-3, D-4, E-3, E-4, F-3, F-4) suggest that, at an initial water equivalent concentration approaching 0.2 w/o, $\text{NOFe}(\text{NO}_3)_4$ forms an anhydrous or partially hydrated (possibly a monohydrate) ferric nitrate which, between 0.2 w/o and 0.3 w/o H_2O equivalent, precipitates a second liquid phase that can yield a crystalline higher hydrate (possibly a trihydrate). Dissolution of this solid hydrate can occur to give another liquid phase on raising the H_2O equivalent to approximately 0.5 w/o.

Attempted Removal of Chloride From N_2O_4

Metallic iron is reported to be nonreactive with liquid N_2O_4 either alone or in mixtures with ethyl acetate, acetonitrile, or dimethylsulfoxide (Ref. 4). Reaction of N_2O_4 with iron is initiated in the

presence of NOCl (Ref. 5) or when a NOCl source such as FeCl_3 plus ethyl acetate (Ref. 6) is present, although the rate is slow at low NOCl concentrations. The FeCl_3 generates NOCl, which is known to react with metallic iron (Ref. 5) to form NOFeCl_4 , which then undergoes solvolysis to give the slow decay compound, $\text{NOFe}(\text{NO}_3)_4$.



The equilibrium (Eq. 7) lies far to the right so that nitrosyl chloride is regenerated and in effect acts as a catalyst for corrosion of the iron.

Thus, the trace amount of NOCl in propellant N_2O_4 was suspected to be the cause of $\text{NOFe}(\text{NO}_3)_4$ formation. Accordingly, an attempt to prepare chloride-free N_2O_4 was made so that a comparative study of the iron corrosion rates (as indicated either by coupon tests, conductivity measurements, or deposition of $\text{NOFe}(\text{NO}_3)_4$ in a dynamic system) could be undertaken. After a single preliminary experiment was completed, together with the development of a suitable analytical procedure, re-orientation of the program objectives led to termination of the study of the effect of NOCl content on the corrosion rate of iron.

An analytical method was developed to ascertain the effectiveness of AgNO_3 as a precipitant for chloride in N_2O_4 , after determining that the large reagent blank (ca. 100 ppm) in the MSC-PPD-2A method for NOCl in N_2O_4 made it unsuitable for very low concentrations of NOCl. The procedure involved hydrolysis of N_2O_4 samples in pure water in an oxygen atmosphere followed by treatment with AgNO_3 and turbidometric determination of AgCl .

A 770-milliliter quantity of N_2O_4 (0.63 w/o NO, 0.03 w/o H_2O equiv, 0.01 w/o NOCl analyzed in accordance with procedures specified in MSC-PPD-2A) was heated in a 1000-milliliter stainless-steel cylinder with 1.0 gram (3.5-fold excess) of finely powdered $AgNO_3$ at ca. 65 C (150 F) for 168 hours. Analytical samples of treated propellant were withdrawn through an integral 40 to 55-micron stainless-steel filter and delivered into tared fragile glass ampoules which were sealed with a torch and weighed. Similarly contained samples of the same propellant without $AgNO_3$ treatment were prepared as a check of the analytical method described below against the MSC-PPD-2A procedure. As a further check a 69.740-gram quantity of the untreated propellant was doped with 0.00252 gram of NOCl (36 ppm) and analyzed as outlined below.

The ampoule containing the N_2O_4 was cooled to freeze the contents and placed in a 500-milliliter iodine determination flask together with 40 milliliters of ice-cooled deionized water. The flask was swept with oxygen for 4 to 5 minutes, stoppered, and shaken to break the ampoule. The glass stopper was sealed with water. After about 15 minutes, the mixture became colorless and it was then heated gently on a hot-plate with frequent shaking to complete the hydrolysis. The solution was filtered through thoroughly prewashed filter paper and diluted to 100 milliliters. To a 25 milliliter aliquot of this solution was added 1.5 milliliters of $AgNO_3$ solution (17 grams/liter), the volume was brought to 50 milliliters, and the solution was aged for 25 minutes in the dark before the absorbance at 535 millimicrons was measured in a 10-centimeter cell. The sample absorptions were converted to chloride concentrations by comparison with a standard calibration curve. The data, shown in Table 9, indicate only a partial removal of the NOCl as $AgCl$ by treatment with $AgNO_3$.

TABLE 9

REMOVAL OF CHLORIDE FROM GREEN N_2O_4

Sample Source	Weight, grams	Cl^- Found, γ^*	NOCl Concentration (cor), ppm
As received	2.524	30	15
As received	2.914	28	11
$AgNO_3$ treated	2.775	22	6
$AgNO_3$ treated	2.841	20	4
NOCl doped	3.174	110	66
NOCl doped	2.980	108	64

*Reagent blank 14 γCl^-

The $AgNO_3$ -treated propellant also was analyzed by the MSC-PPD-2A procedure, which indicated no change in the 0.01 w/o NOCl content.

Analyses for Water Equivalent Concentration in N_2O_4

The MIL-P-26539C method, which depends on the separation (at 1.6 w/o H_2O equivalent) of a second liquid phase during isothermal evaporation of a sample of N_2O_4 at 32 F, has been found unsatisfactory. The analyses listed in Table 10, including comparison of results by different methods, illustrate the problem. The iron materials dissolved in the aqueous phase cause the phase separation method to give an erroneously high value for the water equivalent.

TABLE 10

ANALYTICAL METHODS AND RESULTS FOR H₂O EQUIVALENT IN N₂O₄

Propellant Description and Treatment	w/o H ₂ O Equivalent Found	Analytical Method
As received	0.03	Phase Separation
H ₂ O added to 0.2 w/o; intermittent contact with NOFe(NO ₃) ₄ when hot	0.15 (calculated 0.12 from NO)	Phase Separation
H ₂ O added to 0.2 w/o; stored and contacted with same NOFe(NO ₃) ₄ (now partially hydrated) used above	0.39	Phase Separation
H ₂ O added to 0.2 w/o; heated for 3 days at 150 F in stainless steel	.46, 0.46 0.11	Phase Separation Turner Bulb
Dried, O ₂ treated in glass and distilled from P ₂ O ₅ ; H ₂ O added to part to cause phase separation followed by excess O ₂ ; some of this acid phase plus H ₂ O added to remaining dry N ₂ O ₄	>1.6 1.31, 1.27 (nmr tube shows two phases at 32 F; also similar behavior in tube at 1.0 w/o H ₂ O equivalent)	Phase Separation ¹ H nmr

PHASE II: ENGINEERING EVALUATION

INTRODUCTION

This task was designed to study the effects of various parameters on the rate of precipitation of the metal complex, $\text{NOFe}(\text{NO}_3)_4$, in a bench scale flow system. Successful additives identified in the laboratory study were to be tested for effectiveness and lifetime. The possibility of flow decay in aluminum and titanium systems was to be investigated; also the effect of water, of valve geometry, and of various materials.

EXPERIMENTAL SYSTEM

Flow Bench

An experimental flow bench system was built and used for study of the flow decay phenomenon under contract AF04(611)-11620 (Ref. 1). For this program, although the basic concept of the flow system remained the same, the flow bench itself was completely refurbished with a number of improvements over the old system. In general, smaller and shorter lines, smaller valves, and more insulation were used to reduce thermal lags during start of flow. Improved instrumentation and control were also added.

A schematic of the flow system is presented in Fig. 3. The main tank, or run tank, is contained within a temperature-regulated water bath. Both the main tank and the catch tank are 5-gallon stainless-steel cylinders. The tanks are connected to a pressurization and vent system which maintains both the tank being emptied and the tank being filled at constant pressure during any flow process. All controls, including the setting of pressure levels, are operated remotely.

Two parallel test sections are provided. The flowrate through each is set by a servo-operated remote-control valve. Between each test section and the main tank is a heat exchanger. The heat exchangers consist of a

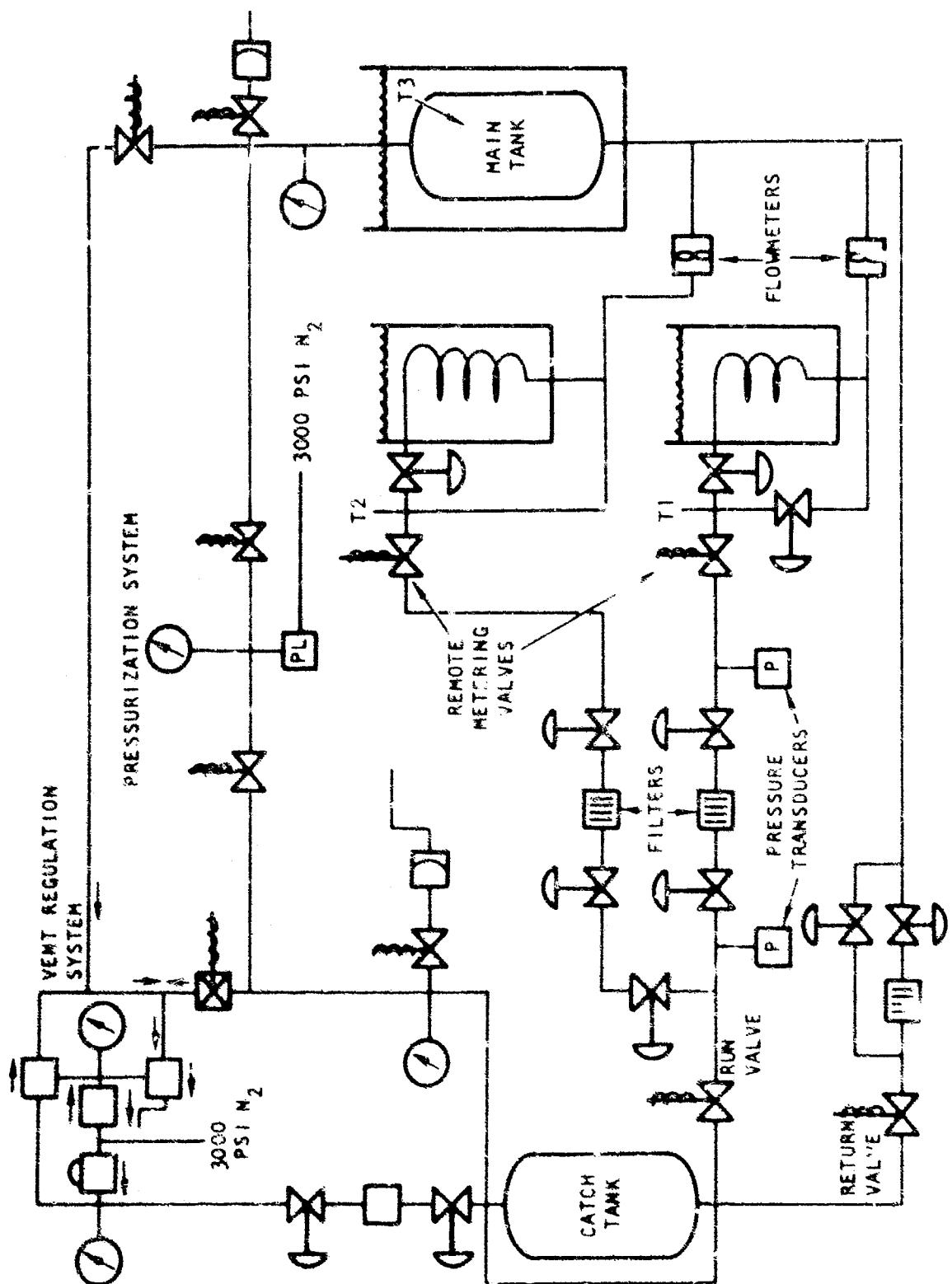


Figure 3. Experimental Flow bench

length of 1/4-inch stainless-steel tubing in an open water bath. Each heat exchanger bath is agitated and the temperature is held constant by an on-off controller which regulates the flow of ice water from a refrigerating bath. A standpipe returns the overflow from the heat exchanger bath to the refrigerating bath. Ball valves are provided to route the flow either through the heat exchangers or around them before entering the test sections.

After completing a run, propellant is recycled to the main tank through a bypass line which can be filtered or not, as desired.

Instrumentation

Nitrogen tetroxide flowrates were measured in each of the parallel test sections by Fischer-Porter radio-frequency-type turbine flowmeters. Propellant temperatures were measured in the main tank and in the line between the heat exchanger outlets and the test sections by iron-constantan thermocouples and a Pace 150-degree reference junction. Pressures upstream and downstream of one test section were determined with two Taber pressure transducers. These flowrates, temperatures, and pressures were recorded on four Hewlett Packard Moseley dual-pen strip-chart recorders.

Pressures in the main tank, catch tank, and pressure regulating systems were observed on bourdon-tube pressure gages.

Heat exchanger temperatures were read directly from the controllers, and the servocontrol units for the metering valves provided an indication of the valve position.

Operating Procedures

Before making a run, the propellant was allowed to soak in the main tank and equalize to the temperature of the surrounding water bath. The heat exchanger controllers were also turned on to bring the heat exchanger

baths to the desired temperature. Final prerun preparations consisted of setting the ball valves in the flow system to achieve the desired flow path.

To begin a run, the main tank was pressurized to the selected level with gaseous nitrogen. The catch tank was then pressurized and the vent regulator set to the proper pressure. Flow was started by actuating the remote-operated ball valve at the catch tank inlet. Individual flowrates through the test sections were adjusted, as necessary, by means of the metering valves.

Most runs were carried to propellant depletion. After the run, the propellant was returned to the main tank through the bypass filter line. The majority of the runs were conducted with a main tank temperature of approximately 125 F and a heat exchanger temperature of about 60 F.

RESULTS AND DISCUSSION

Flow Decay With Dry Propellant

An extensive characterization of the phenomenon of flow decay in "red" or "brown" propellant-grade nitrogen tetroxide (MIL-P-26539A) was reported in Ref. 1. It was found that precipitation of a solid material, identified as $\text{NOFe}(\text{NO}_3)_4$ could be induced by heating N_2O_4 in contact with iron, then cooling prior to, or during flow. This material is extremely adhesive and accumulates at all points of flow constriction such as valves, filters, and orifices.

The solubility limit, in dry propellant, of $\text{NOFe}(\text{NO}_3)_4$ has been shown to be on the order of 1 to 2 ppm as iron. It has also been determined that a positive temperature coefficient of solubility exists. This provides a basically simple mechanism for the occurrence of flow decay. When N_2O_4 has been in contact with iron for a sufficient length of time, a saturated

solution of $\text{NOFe}(\text{NO}_3)_4$ will be produced. Rate-of-solution experiments indicate that equilibrium concentration is reached in no more than a few hours at temperatures of 100 to 120 F. If the solution is then cooled, it will become supersaturated with respect to the flow decay material and ordinary precipitation will occur. Deposits of the material have been obtained by simply flowing hot N_2O_4 past a cold surface (Ref. 1).

Because equilibrium solubility is reached quite rapidly, it is expected that any batch of propellant will contain flow decay material that can be precipitated out by cooling. If the solution is saturated, the amount of cooling necessary for precipitation can be very small. Flow bench runs have been made showing large rates of flow decay with a temperature drop of less than 5 F. Although temperature drop alone is sufficient to precipitate some material, much more precipitate is obtained if the pressure is also decreased during flow. The magnitude of the pressure drop across the constriction in which flow decay is occurring has an important effect on the rate, but the absolute pressure does not appear to be influential (Ref. 1).

The buildup of flow decay deposits is approximately linear with time, regardless of flowrate. Because the total amount of material present is extremely small, only flow systems with a very small cross section to flow will be appreciably affected. Because the underlying process is based on an equilibrium temperature solubility curve, the effects of flow decay are reversible (i.e., if the N_2O_4 is heated rather than cooled while flowing, it will dissolve previously precipitated deposits in valves, filters, orifices, etc.).

At the start of this program, it was agreed that all testing would be limited to the use of "green" propellant (MSC PPD-2A) containing 0.6-percent NO. Therefore, the first task of the flow bench testing was to verify that the same type of behavior as had been observed with brown N_2O_4 would also

occur with the green propellant. The system was loaded with N_2O_4 + 0.6 w/o N_2O + 0.06 w/o H_2O equivalent (PPD-2A) and allowed to soak for 3 days at 110 F. On the first flow run, flow decay was procured in the test orifice. This is in contrast to the experience on the previous program where approximately 3 weeks of operation were required before flow decay appeared spontaneously. One important factor is that in this case the tanks were not new; the tanks from the previous flow bench were cleaned and reinstalled.

Typical flow decay behavior with the green propellant (PPD-2A) is presented in Fig. 4. The effect is seen to be temperature reversible. After previous runs with propellant flowing through the heat exchanger had resulted in partial plugging of the metering valve, the heat exchanger was bypassed during run 64 and the hot N_2O_4 dissolved the solid deposit. It should be noted that the soak temperature of the propellant was 116 F and the temperature of the propellant flowing through the test orifice was 113 F, a measured 3-degree decrease in propellant temperature. At first glance these results appear anomalous in light of the above discussion. They are, however, completely consistent with physical chemical principles; i.e., solubility equilibrium is reached quite rapidly (Ref. 1) between the tank walls and the propellant adjacent to the tank wall (with respect to the soluble iron species). In a relatively large-volume quiescent system under isothermal conditions, the diffusion of the soluble iron species from the propellant adjacent to the tank wall to the bulk of the propellant is necessarily a slow process.

The maximum concentration gradient, which provides the only driving force under isothermal conditions to achieve complete equilibrium with respect to the soluble iron species, is something less than that caused by a differential concentration of 2 ppm in terms of iron. Although the exact molecular structure of the soluble iron species has not been ascertained, it must be relatively heavy on the atomic scale resulting in a proportionately low diffusion coefficient.

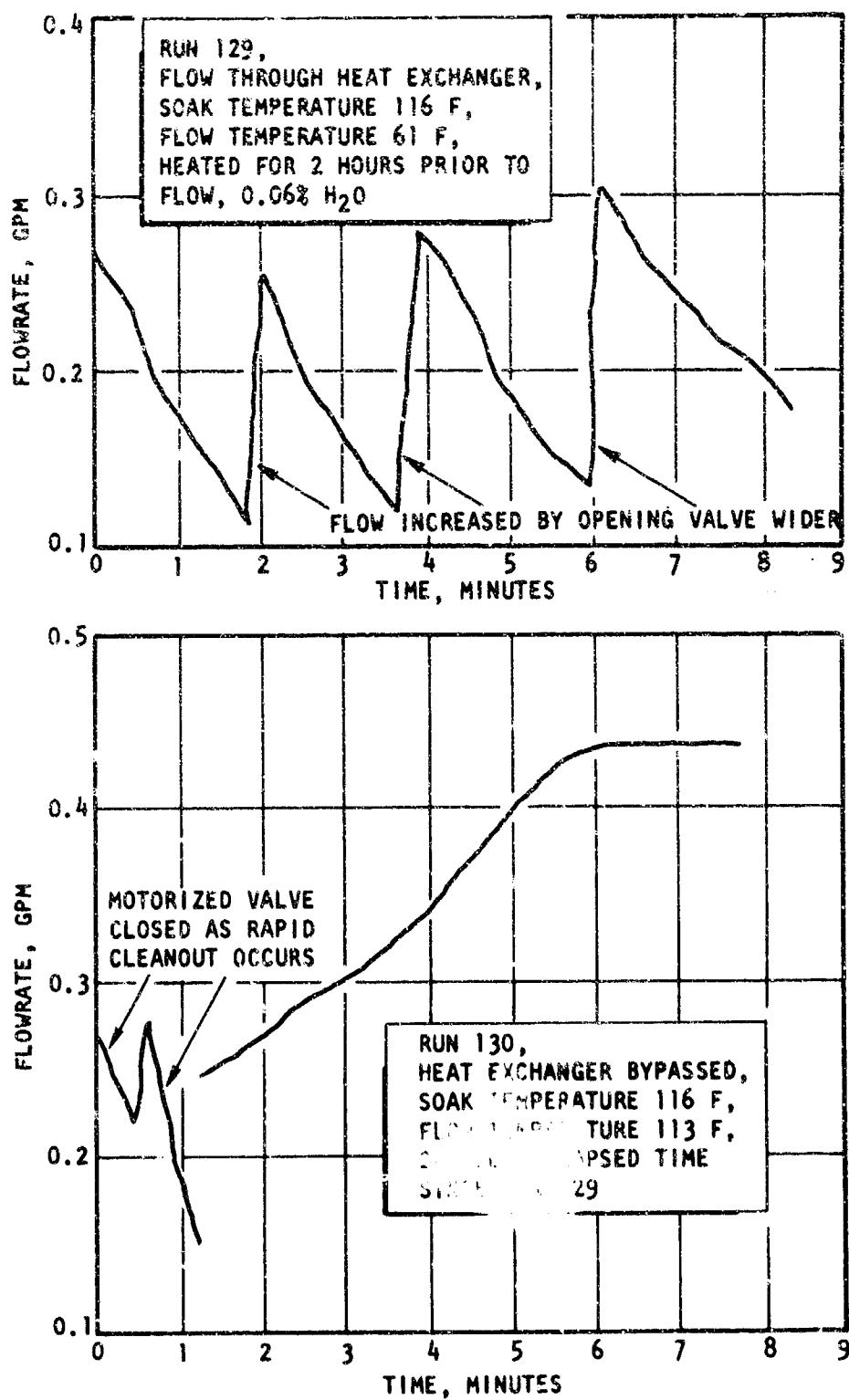


Figure 4. Flow Decay and Cleanout in Valves With PPD-2A Propellant

On the basis of the measured data and the above discussion, it is apparent that the bulk of the propellant had not achieved equilibrium with regard to the solubility of the iron species after a 24-hour soak at 116 F. As a result, the solubility of the iron species in the flowing or mixed propellant (i.e., the bulk of the propellant plus the propellant adjacent to the tank walls) was not exceeded at the flow temperature 113 F. As a consequence, the deposit in the valve dissolved. The experimental results were similar to those obtained on many runs with brown N_2O_4 , MIL-P-26539A/B (Ref. 1). After making several flow bench runs with varying experimental conditions, it was concluded that the behavior of N_2O_4 , as defined by the MSC-PPD-2 specification which contains 0.06 w/o water equivalent, was identical in all respects to that of brown N_2O_4 as specified in MIL-P-26539B which contains less than 0.1 w/o water equivalent.

Effect of Water

Analysis in accordance with procedures specified in MSC-PPD-2A of the bulk propellant used in this program indicated a water content of 0.06 w/o, approximately the same as that of the brown propellant used in the previous program. Although it had been suspected that water concentration might be a variable of interest, there was no evidence to suggest that flow decay behavior would be influenced in any particular way by changing the water content. However, it was felt that high concentrations of water would provide the most unfavorable conditions because of the known increase in corrosivity of N_2O_4 with increase in water content. Therefore, it was agreed that the flow bench tests would be conducted with propellant containing 0.2-percent water, the upper limit of the use specification.

After establishing baseline behavior with the as-received propellant containing 0.6-percent N_2O_4 and 0.06-percent H_2O , water was added to the flow bench to increase the water content to about 0.2 percent. Succeeding runs produced no evidence of flow decay behavior. This result was totally unexpected. Propellant samples were then removed from the flow bench and reanalyzed. The analysis showed a water content of about 0.44 percent. Attempts were made to discover the source of the excess water, but analysis

confirmed that neither the bulk N_2O_4 supply nor the nitrogen pressurant, the only other system input, were excessively wet. It was then postulated that water from the temperat re-control baths surrounding the main tank and the heat exchangers somehow contaminated the system over a period of time.

The flow bench was emptied, purged, and reloaded with propellant. Flow decay reappeared immediately. Then a number of runs were made to see if the water concentration would change with time. However, the analytical results were constant at 0.06-percent water. Water was then added as before, to bring the concentration up to 0.2 percent. After thoroughly mixing the propellant by recirculation, a sample removed from the system yielded an analysis of 0.39-percent water. At about this time, a series of similar experiences in the laboratory effort confirmed the obvious conclusion: the phase separation method for water analysis can give highly incorrect results when the propellant has been heated and/or saturated with iron corrosion products (see section on Laboratory Effort).

Although the water analysis was shown to be inaccurate, the original flow bench observation remained as before: increasing the water content from 0.06 to 0.2 percent in a system experiencing flow decay through a valve results in the elimination of flow decay. The flow decay deposits are removed and flowrate is completely recovered. In this respect, water at first appeared to be as effective an additive in preventing flow decay as those discovered in the previous effort (Ref. 1). However, the observation of gelatinous or viscous liquid deposits in wet propellant in the laboratory soon led to the following hypothesis: The addition of water to the system converts $NOFe(NO_3)_4$ to a gel-like material as observed by TRW (Ref. 2) in their flow bench experiments. This material will not stick to or clog a valve, but would be removed by a filter.

To test the above hypothesis, a flow bench experiment was set up with a needle valve in one side of the parallel flow circuit and a filter in the other. The filter was stainless steel, with a 2- to 5-micron pore

size. The valve setting was adjusted to provide the same initial flow-rate through valve and filter with a pressure drop of 60 psi. A fresh load of propellant was placed in the flow bench and "normal" flow decay behavior observed. Flowrates through both filter and valve decreased slowly with time. Then water was added to the system to bring the concentration up to 0.2 percent. On the following run, the deposits in the valve were immediately removed; flowrate in this arm of the test section returned to its initial value and remained steady for the duration of the run. The filter, in the other arm of the parallel flow circuit, with inlet and outlet conditions identical to those for the valve, showed a higher rate of flow decay than before. These two runs are shown in Fig. 5. It should be noted in run 36 that the metering valve (i.e., the test orifice) had to be closed sharply to maintain flow within the desired range. The conversion of the crystalline $\text{NOFe}(\text{NO}_3)_4$ to another form, presumably a viscous liquid or gel-like material, is extremely rapid under these experimental conditions.

In repeated runs over a 2-week interval after the addition of water, no flow decay through the valve was observed. Deposits continued to accumulate on the filter, but at a very low rate as compared to the first run after water was added. Later runs were made with hot propellant flowing through the filter, bypassing the heat exchanger. It was found (Fig. 6) that hot N_2O_4 dissolved the filter deposits; thus the deposition of gelatinous material on filters in wet N_2O_4 is temperature reversible, as is the deposition of solid $\text{NOFe}(\text{NO}_3)_4$ in dry N_2O_4 . As discussed previously, the propellant had not reached equilibrium with respect to the soluble iron species. In this instance, a soak time of only 1.5 hours was used and the gel-like deposit dissolved when exposed to hot propellant. This suggests that an equilibrium solubility is involved in both cases, with the nature of the insoluble material being a function of the water content of the propellant.

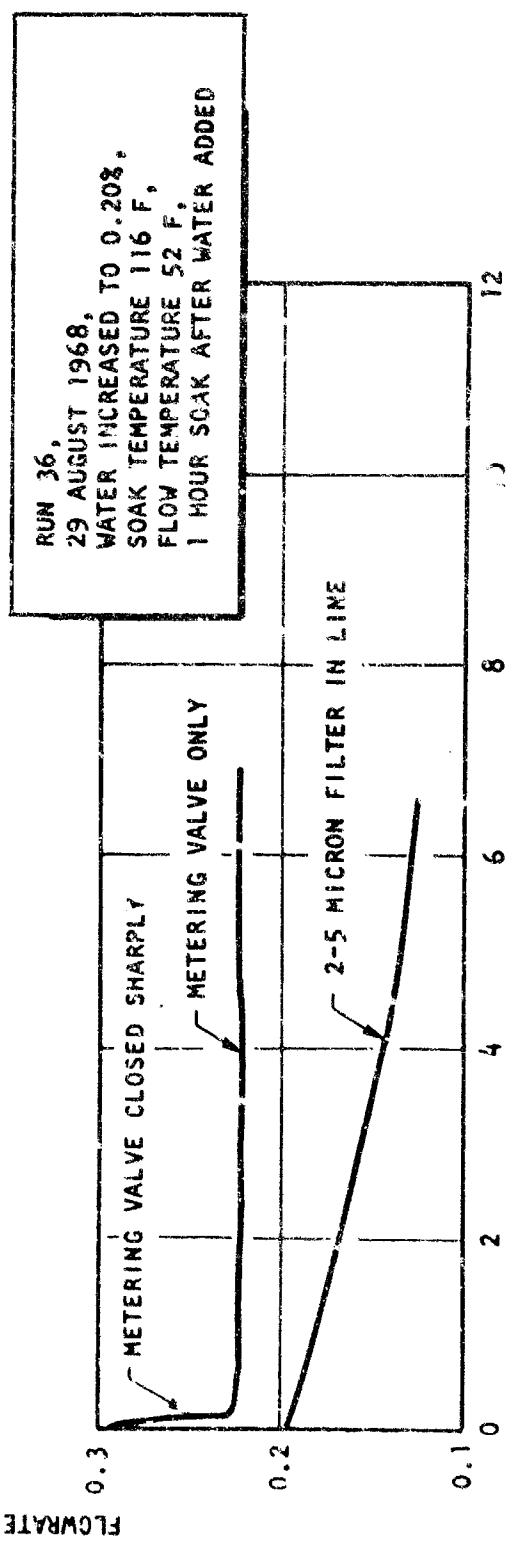
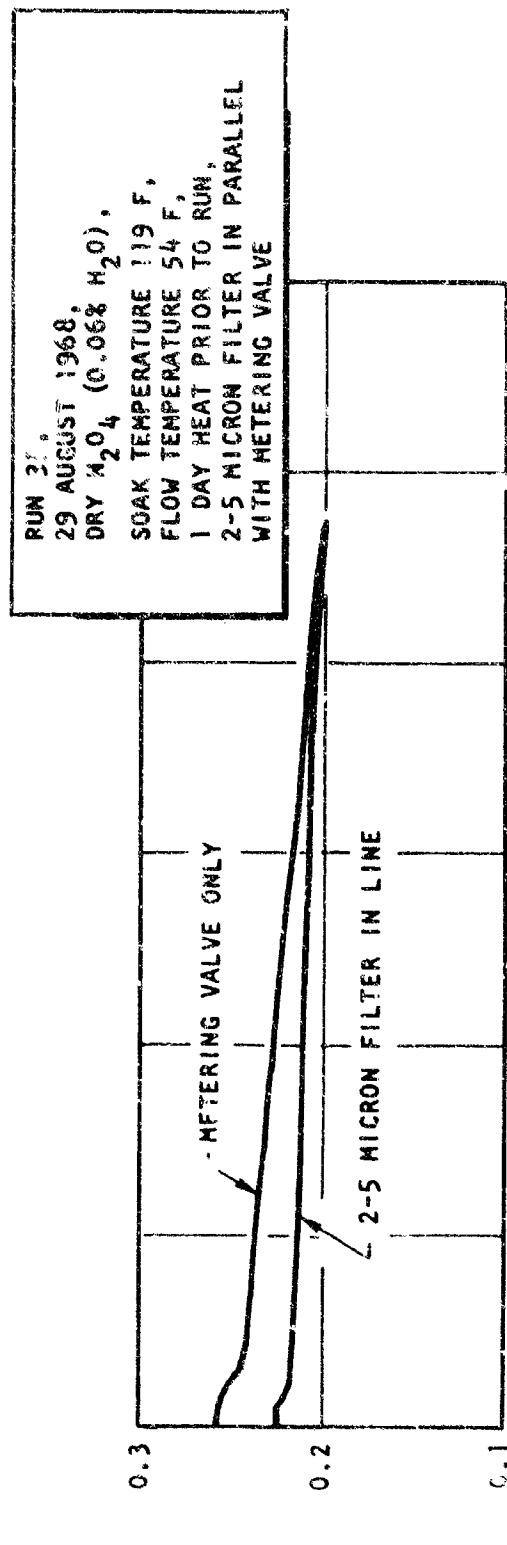


Figure 5. Effect of Water

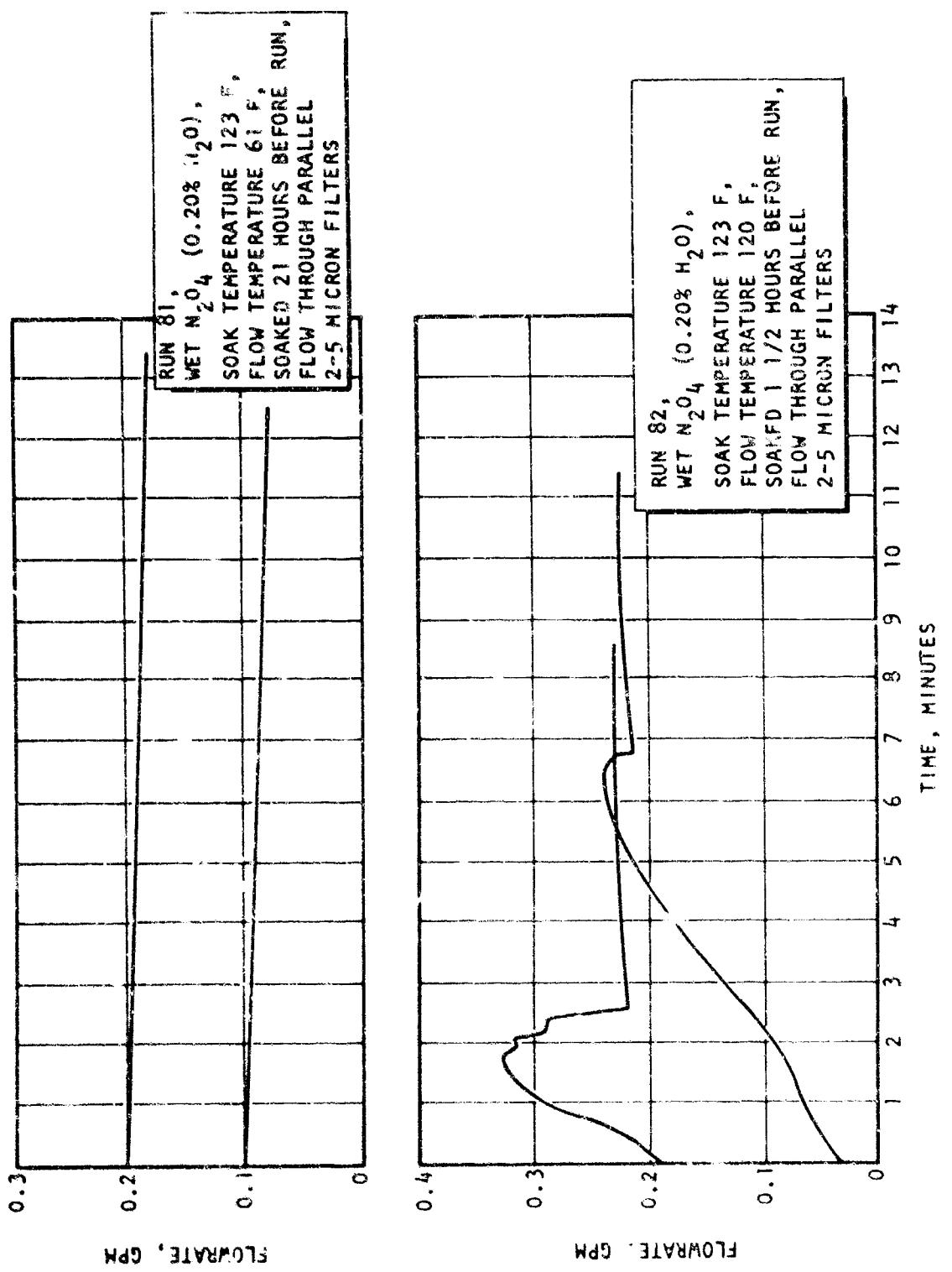


Figure 6. Flow Decay and Temperature Reversal in Filters With Wet N_2O_4

All the above experiments were repeated over a 2-month period with identical results. The dimensions of the flow decay problem, as perceived at the beginning of this program, were thus greatly changed. Instead of a single, well-characterized deposit, at least two entirely different types of deposit are formed, depending on water concentration.

Filter Effects

Because the deposits formed in N_2O_4 containing 0.2-percent water do not adhere to normal valves and orifices, it was impossible to use the experimental techniques which were used in studying the deposition of $NOFe(NO_3)_4$. It was necessary to use filters instead of valves as the test restriction for detecting the occurrence of flow decay. This caused certain difficulties in flow bench experimentation because flow area through filters cannot be adjusted easily as it can with valves. The design principle on which the flow bench operates requires that the pressure drop across the test restriction be at least of the same order of magnitude as the pressure loss through the rest of the flow system. If it is not, then small changes in the flow area of the test restriction, due to flow decay deposits, will not appear as significant changes in flowrate through the bench system.

The filters used in this study were made of sintered 303 stainless steel, with a thickness of approximately 0.060 inch. The five different pore sizes used were 2-5 (2 micron nominal, 5 micron absolute), 5-9, 10-15, 20-30, and 40-55 microns.

Runs 78 and 79 (Fig. 7) illustrate the behavior of flow decay in 2-5 micron filters using dry propellant. The flow traces resemble those obtained with a valve as the test restriction, but the decrease of flowrate with time is less linear and not as reproducible on succeeding runs. When the water concentration was increased to 0.2 percent, resulting in

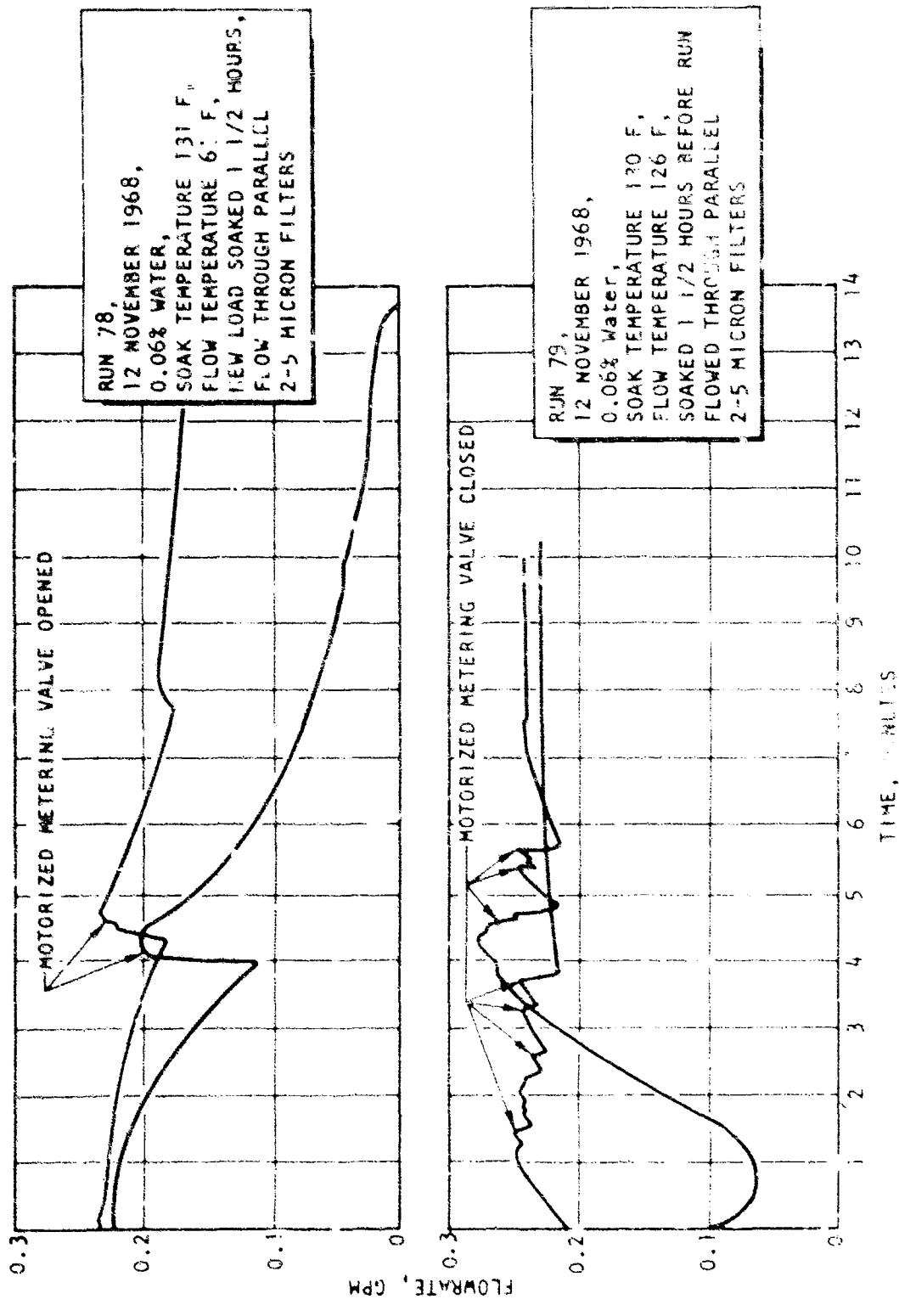


FIGURE 7. Flow Decay and Cleanout at Filters with Dry Na_2O_4

as a change in the characteristics of the deposit produced, the experimental behavior became less reproducible and harder to analyze. It was generally observed that the first run after adding water produced an appreciably larger rate of flow decay than immediately succeeding runs. This is illustrated by the data for the 2-5 micron filter in Fig. 8. It would have been impractical to conduct every run with a new load of propellant to obtain the higher, more useful rate of flow decay on each run. Therefore, it was necessary to try to compare data from runs showing small and nonreproducible rates of flow decay.

The material deposited from wet N_2O_4 in the first filter experiment (Fig. 5) did not clog the valve which was in parallel with the 2-5 micron filter. This suggested that it might be possible that a filter could be found with a pore size large enough to let the gelatinous flow decay deposits pass through, but still small enough to perform most necessary filtering functions. Baseline runs with two 2-5 micron filters in parallel varied appreciably but showed approximately the same magnitude of flow decay in each (Fig. 6). One of the filters was then changed to the largest pore size available, 40-55 microns. Parallel runs then gave the same decay rate as before in the 2-5 micron filter, but no discernible flow decay in the side with the 40-55 micron filter. An uncontrollable parameter in this experiment was the pressure drop across the filter. Because the pressure drop through the large-pore-size filter was much smaller, a valve upstream of this filter adjusted the system flowrate and pressure drop to be the same in both circuits.

The above experimental arrangement resulted in the type of unsatisfactory condition discussed earlier; small amounts of deposit on the large-size filter would not cause appreciable changes in flowrate. Therefore, the experiment was repeated using a 40-55 micron filter with only one-tenth the surface area. In this case, flow decay was observed at approximately the same rate as for the 2-5 micron filter (Fig. 8). For filters in this size range, it appears that the rate of decrease in flow area through the filter is independent of the size of the individual pores.

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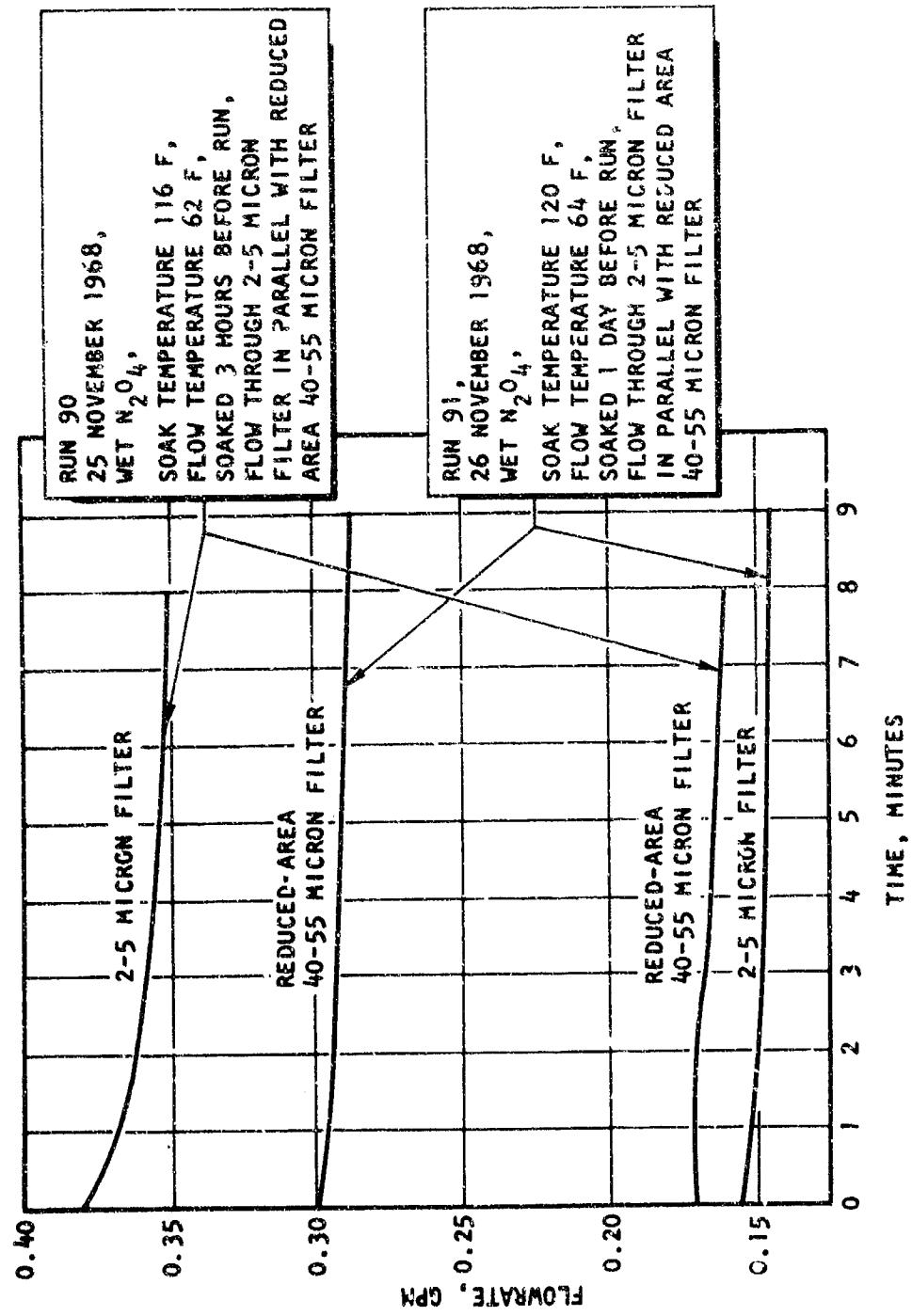


Figure 8. Flow Decay in Two Filters With Wet N_2O_4

An attempt was made to determine quantitative relationships between filter size and area and the magnitude of flow plugging to be expected in a given system. Data from filters with different pore sizes were correlated by means of the flow coefficient, C_v , defined as:

$$C_v = \text{flowrate} \times \frac{\text{liquid specific gravity}}{\text{pressure drop across filter}}$$

Figure 9 is a plot of the observed C_v values for a series of runs with different filters. The abscissa on this graph is the volume of propellant flowed through a filter divided by the surface area of the filter. All runs were made with two filters in parallel having different pore sizes. The total run time remained approximately constant, so that the filters with the smallest C_v values had a smaller quantity of propellant flowed through them. As flow decay deposits accumulate on the filter, the cross section available for flow is reduced, and the effective C_v is reduced. When changes in C_v values due to flow decay deposits are given, it is then possible to compute either the decrease in flowrate which would occur in a constant pressure system, or the increased resistance and its effect on flow in a pump-fed system.

The objective of plotting the data in this fashion was to make it possible for a system designer to select a filter pore size and be able to compute the filter area needed for a given total quantity of propellant, to keep the possible effects of flow decay within the specified limits. However, the data obtained were not reproducible and consistent enough to develop definite quantitative relationships. For instance, run 134 showed approximately the same rate of flow decay in a 2-5 micron filter as in a 10-15 micron filter, but in run 138 the 10-15 micron filter showed a higher rate of flow decay. This nonreproducibility of rates made it impossible to make meaningful comparisons between filters on individual runs. The data in Fig. 9 show clearly that, the smaller the initial C_v for a filter, the higher the probability that it will be subject to flow decay when used to filter a given volume of propellant.

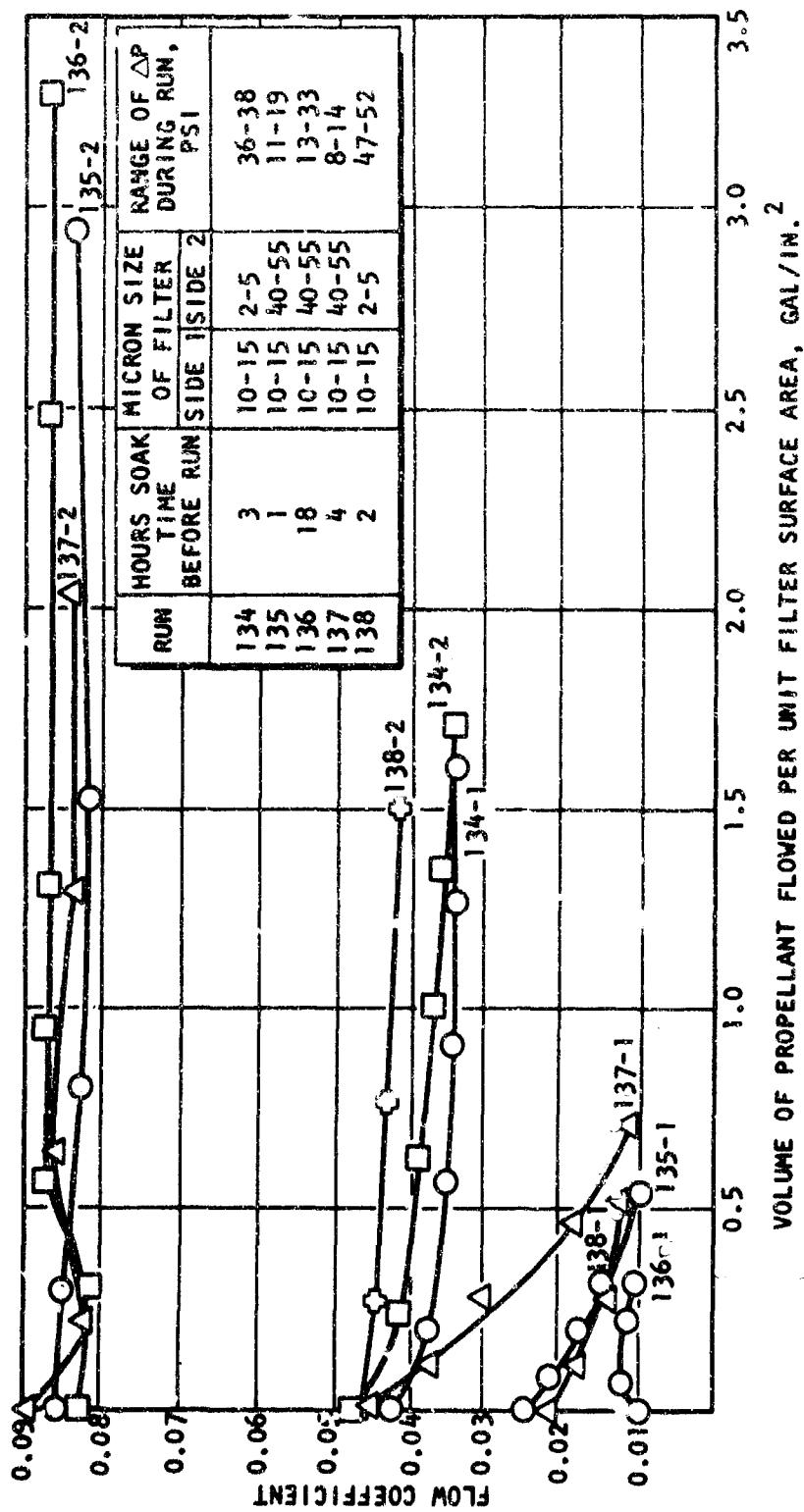


Figure 9. Flow Decay in Filters With Wet Propellant

Therefore, filter pressure drops should always be kept as low as possible. If filter size or area is fixed by other constraints, then the flow coefficient should be as large as possible (which usually, though not necessarily, means using the largest pore size which is acceptable).

Additive Effects

The primary objective of this program was to demonstrate the elimination of flow decay through the use of chemical additives. After discovery of the effect of water in changing the nature of the flow decay deposits, it was soon found that the additives which had previously proved effective in dissolving $\text{NOFe}(\text{NO}_3)_4$ were not able to dissolve the gelatinous or viscous liquid deposits obtained from $\text{N}_2\text{O}_4 + 0.6\text{-percent NO} + 0.2\text{-percent H}_2\text{O}$. Therefore, a search for new additives was conducted in the laboratory effort and two of the materials tested were carried into flow bench tests.

Picric Acid. Although it was not effective in dissolving the liquid deposits, picric acid (2,4,6-trinitrophenol) was observed to cause a crystallization of the liquid. This did not provide the hoped-for prevention of deposits, but it was thought that the characteristics of the crystalline material might be such that it would not cause plugging of the filters. If a porous filter cake were produced, the effect on system flowrate might be negligible even though substantial quantities of the material were present on a filter. With this in mind, 0.25 weight percent of picric acid was added to a new load of N_2O_4 and allowed to heat in the main tank overnight. The first flow run was made with a 2-5 micron filter in parallel with a reduced-area 40-55 micron filter, both of which contained some flow decay deposit from a previous run. The result was a flow decrease across both filters (Fig. 10). Midway through the run, flow was switched to bypass the heat exchanger and send hot propellant through the filters. At first, flowrate sharply increased, indicating a dissolving of the deposit; but then flowrate again began to

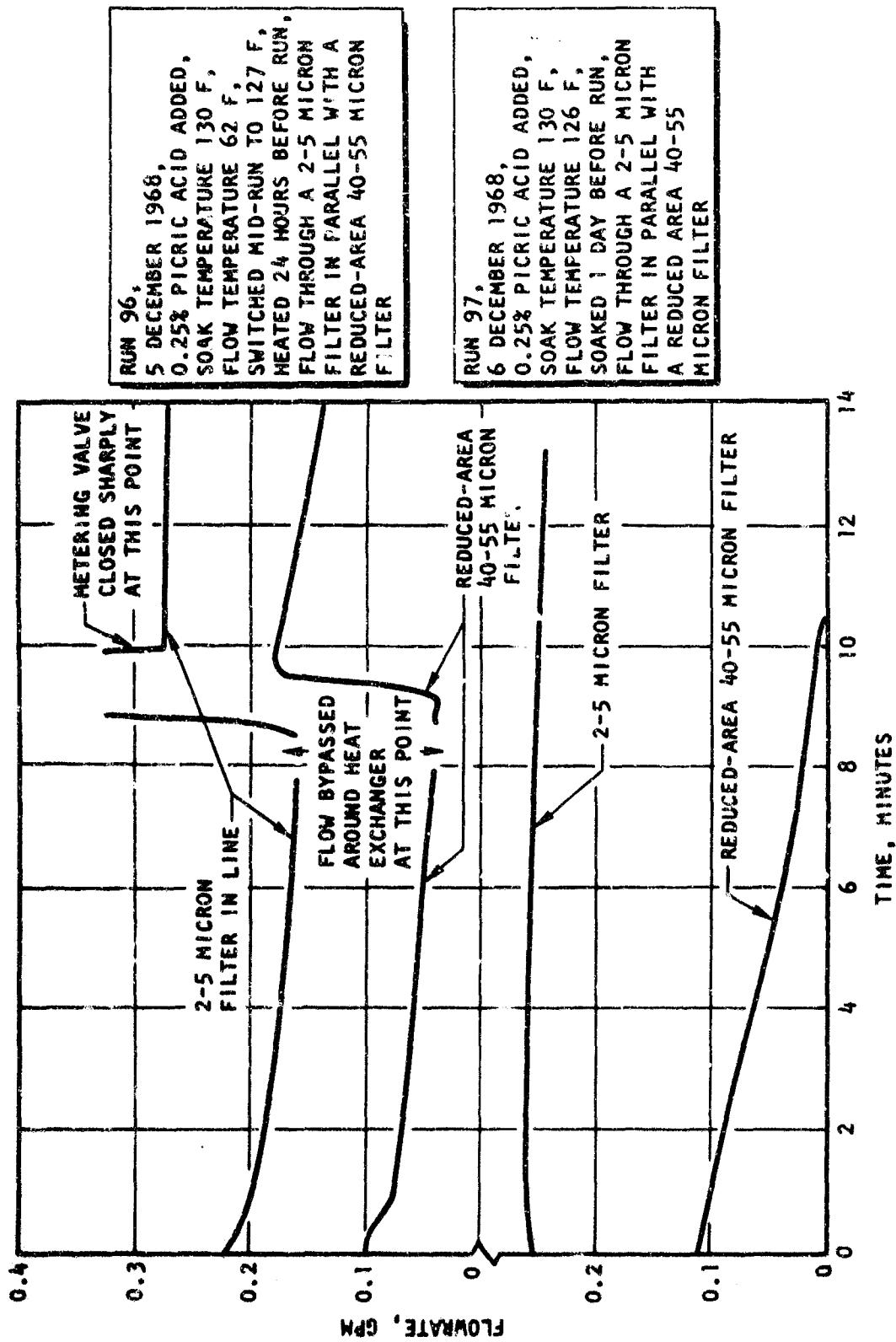


Figure 10. Flow Decay With Picric Acid Additive

drop, particularly in the reduced-area filter. These results appear to correspond to the laboratory observations, where only a part of the deposit was affected by picric acid and the remainder was soluble in hot propellant. Thus, on bypassing the heat exchanger, the unaffected portion of the deposit was first redissolved, then additional precipitation of the picrate caused flowrate to decrease again. Additional runs resulted in more deposition and a further decrease in flow (Fig. 10).

Next, water was added to the system to bring the concentration to 0.2 percent. Following runs showed no significant increase or decrease in the flowrate. The filter deposits did not redissolve as when water is added to a system with deposits of solid $\text{NOFe}(\text{NO}_3)_4$. When the filters were removed for cleaning, a thick layer of yellow solid was observed on the 2-5 micron filter, but none on the 40-55 micron filter. It is possible that the plugging of the larger filter occurred within the pores rather than on the surface.

The flow bench was emptied and reloaded with propellant. This time the propellant was first brought to 0.2-percent water content before adding the picric acid. The behavior observed was essentially the same as previously when the picric acid was added before the water. Flow runs were made with a 2-5 micron filter in parallel with a needle valve. On the first run, flow through the filter decreased sharply, but the valve was unaffected. Succeeding runs over a period of 2-1/2 weeks showed no appreciable further deposition in the filter. These data suggest that picric acid in wet N_2O_4 forms an insoluble precipitate with any flow decay material in solution, but then inhibits the formation of additional material from the tank wall. Thus, the use of picric acid as both an additive and a passivation or pickling treatment might prevent flow decay. If picric acid were added to a system, and the propellant then filtered to remove the precipitate initially formed, flow decay might not occur in that system as long as some picric acid remained in the propellant.

After completing the second series of runs with picric acid, the flow bench was emptied and reloaded with new propellant adjusted to 0.2-percent H₂O. The first three runs, with a 10-15 micron filter, exhibited a moderate rate of flow decay. However, the next few runs showed increasing flowrates, both when going through the heat exchanger and when bypassing it. It was hypothesized that this behavior was due to an inhibiting layer formed on the tank wall by picric acid in the previous experiments and the addition of fresh propellant without picric acid shifted the solubility equilibrium. Therefore, the system was again emptied and washed with deionized water. After drying and refilling with propellant, normal behavior was restored.

Dimethylsulfoxide. Dimethylsulfoxide (DMSO) was observed to dissolve liquid flow decay deposits from wet propellant in the laboratory depositor. It was the only material discovered to do so. Before testing DMSO in the flow bench, a new load of propellant (N₂O₄ + 0.6-percent NO + 0.2-percent H₂O) was placed in the bench and flow decay demonstrated with a 2-5 and a 10-15 micron filter in parallel (run 143, Fig. 11). Then 0.25-percent DMSO was added to determine whether the previously deposited material would dissolve. Instead of flow recovery, sharp flow decay was observed in both filters (run 144, Fig. 11). Switching the flow to bypass the heat exchanger did not dissolve the deposits. Additional runs continued to reveal flow decay.

A new batch of propellant was then loaded into the flow bench and water and DMSO added. Again, flow decay appeared, both when flowing through the heat exchanger and when bypassing it. A third propellant load also produced the same results.

At this time, the flow bench was again emptied and then reloaded with dry propellant. Only a moderate rate of flow decay was obtained with the dry propellant; a second load also failed to show the strong flow decay normally observed in previous batches on the first run. These results may indicate that a passive film was formed.

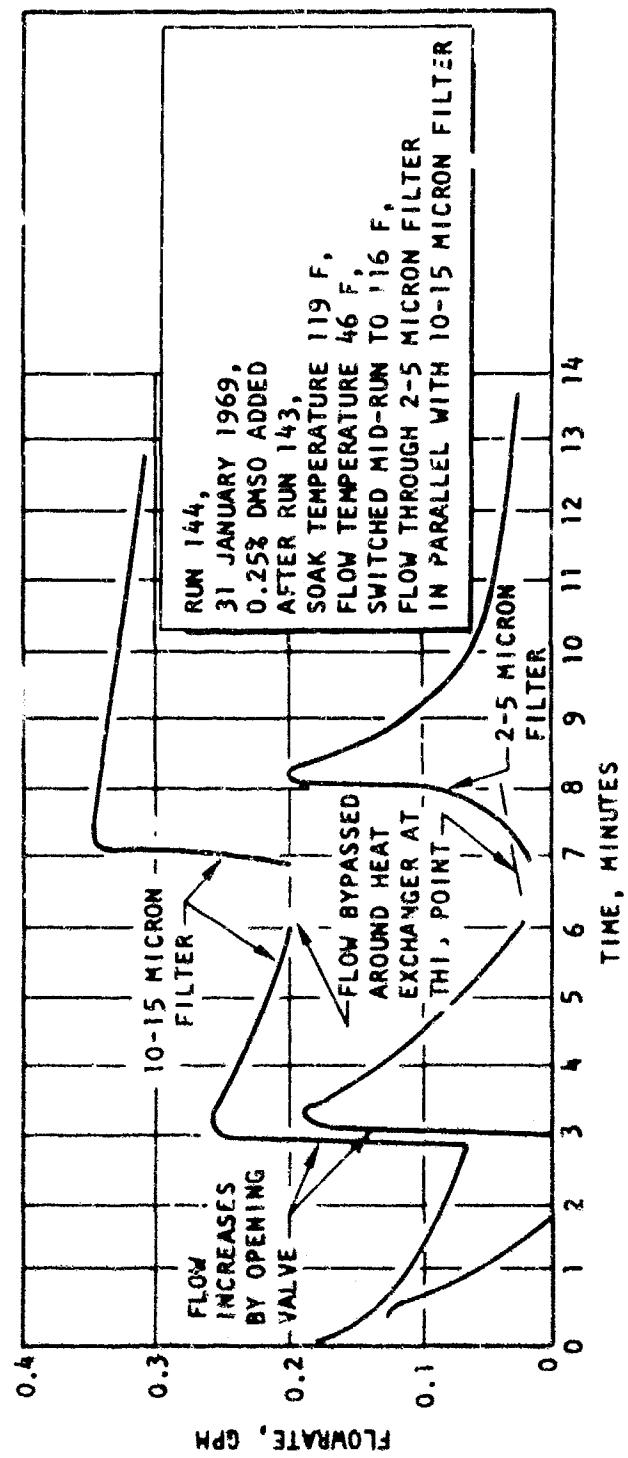
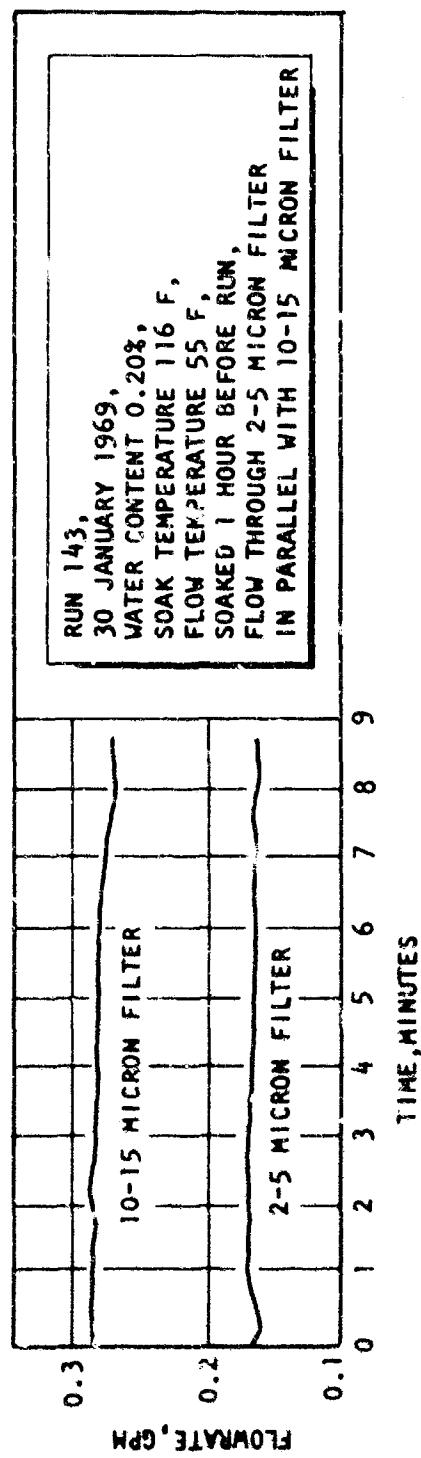


Figure 11. Effect of Dimethyl sulfoxide on Flow Decay

No satisfactory explanation could be found for the failure of DMSO to dissolve the flow bench deposits as it had in the laboratory depositor. This was the only instance in which laboratory observations could not be confirmed in the flow bench. A final flow bench run again resulted in flow decay with 0.2-percent water and 0.5-percent DMSO.

Coupon Corrosion Tests

The objective of this task was to compare the corrosivity and materials compatibility of PPD-2A propellant with those of the same propellant containing the chosen additive to prevent flow decay. Materials chosen for testing included aluminum alloys 2219, 6061, and 2014, stainless steel 347 titanium 6A-14V, maraging steel 250, Teflon, and Kynar. Test samples were cut into disks 13/16 inch in diameter and 1/16 inch thick. These specimens were strung on Teflon rods and separated by Teflon spacers. To further minimize interaction between specimens, Kel-F disks 7/8 inch in diameter by 1/16 inch thick were placed between the specimens on the rods and separated by Teflon spacers. Sample bombs were made of sections of 1-inch tubing to house the assembled specimen rods. Stainless-steel valves, tubes, and caps were used for the stainless steel, maraging steel, titanium and Kynar samples. Aluminum valves, tubes, and caps were used for the aluminum and Teflon specimens. Enough material specimens and sample bombs were provided to allow testing of three additives, for three different exposure time-temperature combinations, with both liquid and vapor exposures and duplicate samples for every test condition.

Analysis of the bulk propellant yielded a composition of 99.05-percent N_2O_4 , 0.57-percent NO, and 0.05-percent H_2O . Water was added to bring the concentration up to 0.2 percent.

Before discovering the effect of water on the nature of the flow decay deposits, acetonitrile was considered to be the most effective chemical additive found. Therefore, the first set of long-term coupon tests were initiated with 0.25-percent acetonitrile and an untreated propellant blank.

After the laboratory effort showed that acetonitrile could no longer be considered an effective additive, the coupon tests were terminated without analysis of the results. Corrosion tests for the additives picric acid and dimethylsulfoxide were not conducted because of the unsuccessful results obtained in the flow bench.

Flow Decay in Aluminum and Titanium Systems

A small flow bench system was constructed for experiments to determine whether partially soluble metal complexes would form as corrosion products in aluminum and titanium tankage, and would then precipitate in valves and filters to cause flow decay.

Flow Bench and Instrumentation. Three separate flow systems, one using stainless-steel tanks, one titanium tanks, and one aluminum tanks, were built and enclosed in a temperature-regulated oven. A flow schematic is presented in Fig. 12. Each flow system consisted of a main soak tank, a run line, a flowmeter, a heat exchanger, a flow-control needle valve, a filter if desired, and a catch tank. The tank volumes varied between 1 and 1.5 gallons. The stainless-steel and aluminum tanks were new, but the titanium tanks had been used previously for housing N_2O_4 stress corrosion samples. Piping and valves for all systems were stainless steel.

Both the main tank and catch tank could be maintained at a constant pressure or vented at fixed pressure during a run. Four thermocouples monitored the temperature at various points in the oven. Flowrates were measured with a Fischer-Porter RF-type turbine flowmeter and read out on a strip-chart recorder.

The oven was maintained at a constant temperature of approximately 120 F. To make a run, the main tank was set to the selected pressure and the catch tank to the desired vent pressure. The heat exchanger coils were

PRESSURE AND VENT REGULATION SYSTEMS

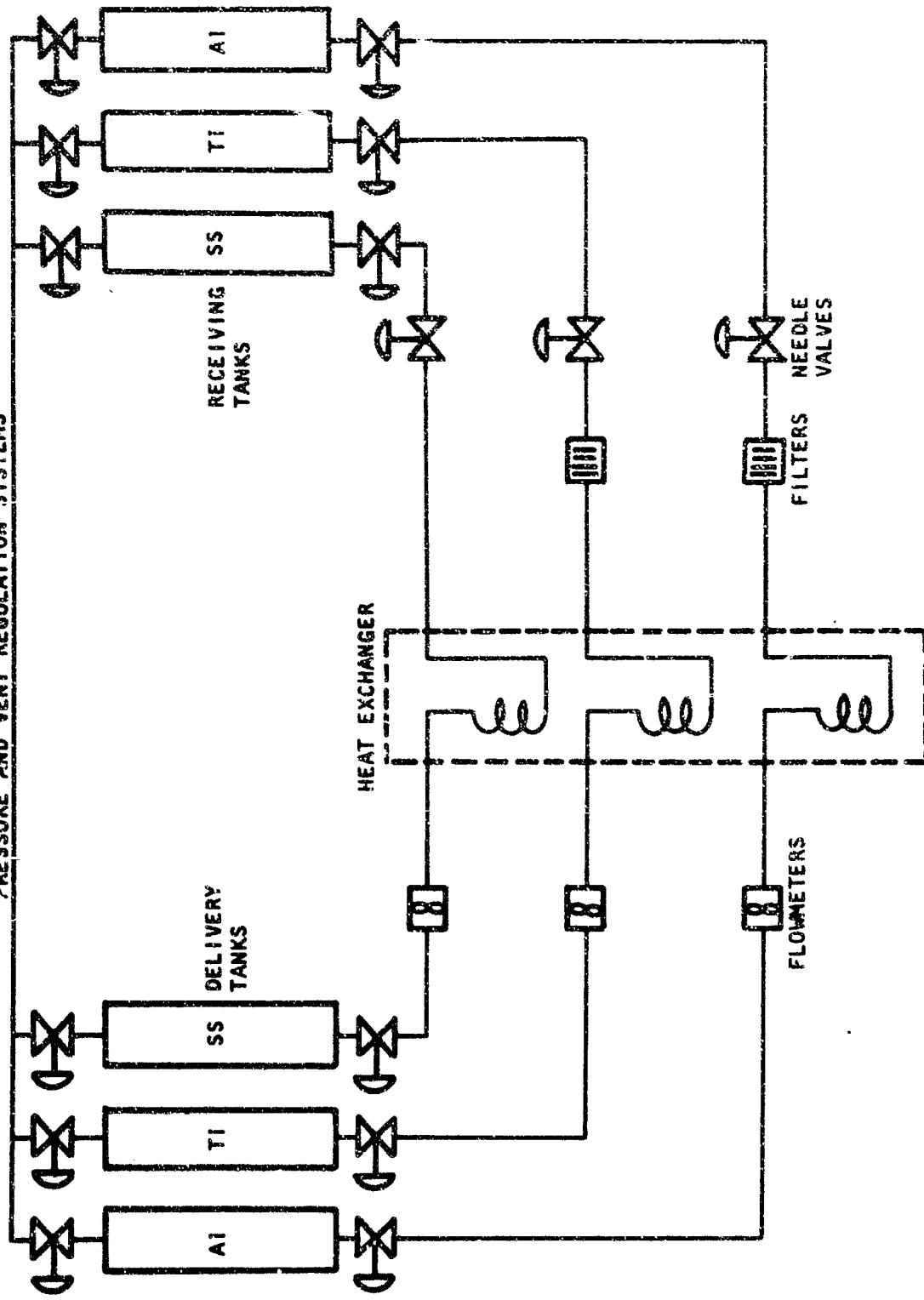


Figure 12. Aluminum, Titanium, and Stainless-Steel Parallel Flow System

cooled with running tap water. Flowrate through the system was adjusted manually with the needle valve to about 0.1 gpm. At the end of a run the catch tank was pressurized, the main tank vented, and the propellant returned to the main tank via the run line and heat exchanger.

Discussion of Results. After loading with as-received propellant (0.06-percent water content) and soaking for approximately 2 weeks in the oven, a flow run was made with each of the systems. Flow decay across the needle valve appeared immediately in the stainless-steel system but not in the aluminum or titanium systems.

On the third set of runs, after a total soak time of 4 weeks, the aluminum and titanium systems were each fitted with a 5-9 micron filter downstream of the heat exchanger. The following run exhibited a sharp rate of flow decay in both systems, as well as in the stainless-steel system which did not have a filter (Fig. 13). The filters were then removed for analysis of the deposits. No deposits were visible on the surface of the filters. Analysis of the filter washings by emission spectroscopy indicated the presence of titanium in the titanium system but no aluminum in the aluminum system. However, it was suspected that the extraction procedure might have allowed the loss of the aluminum precipitate.

The filters were cleaned and replaced in the system. Succeeding flow runs again produced an appreciable rate of flow decay. The filters were removed and extracted with ethyl acetate. The solvent was then evaporated and the residue analyzed as before. Table 11 shows the results of the analysis.

TABLE 11
RESIDUE ANALYSIS

Constituent Found in Residues	5-9 Micron Filter Used in Aluminum System	5-9 Micron Filter Used in Titanium System
Al, percent	0.071	0.029
Ti, percent	0.18	0.49
Fe, percent	>4.9	>10.5

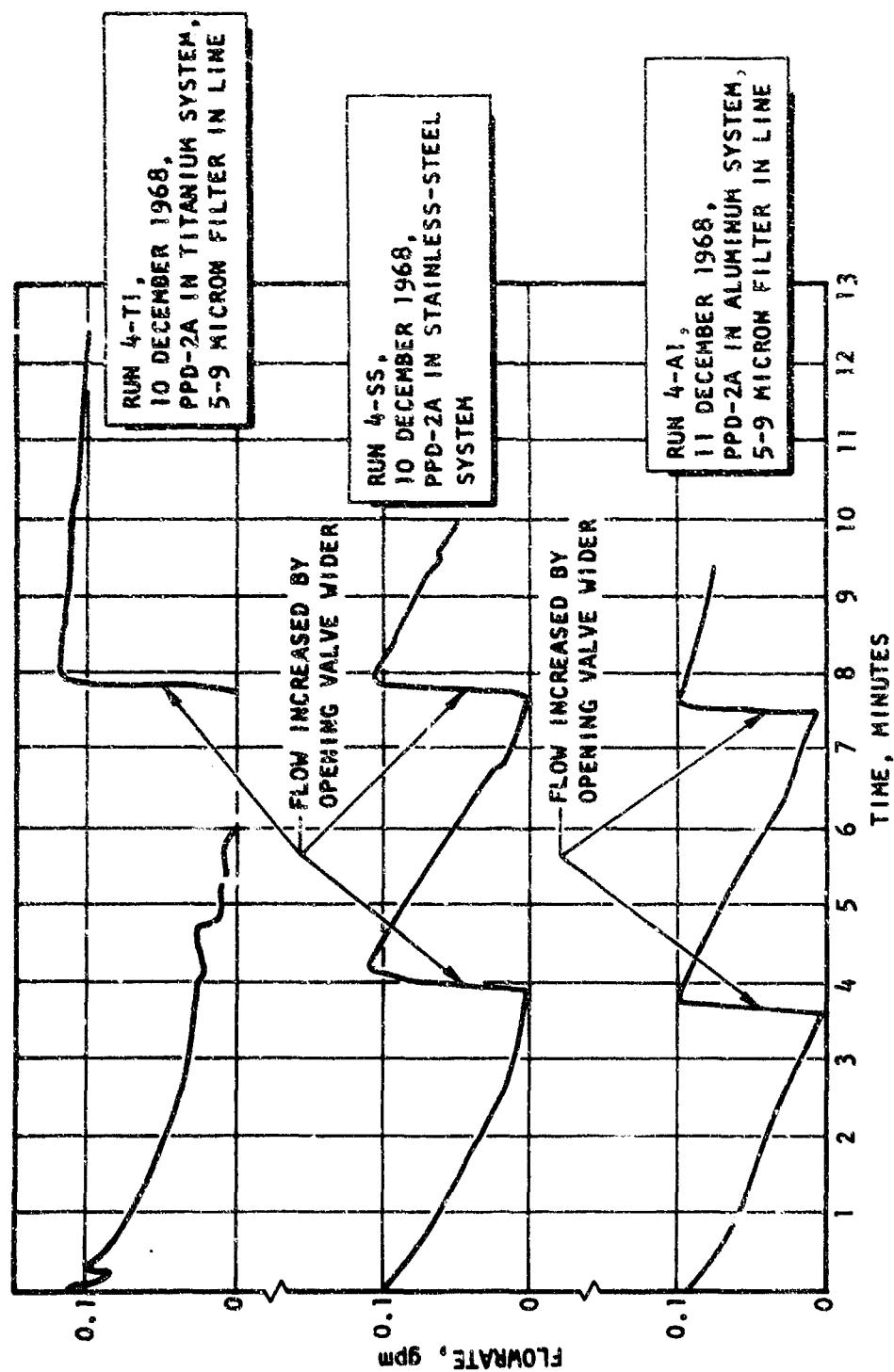


Figure 13. Flow Decay in Aluminum, Titanium, and Stainless Steel

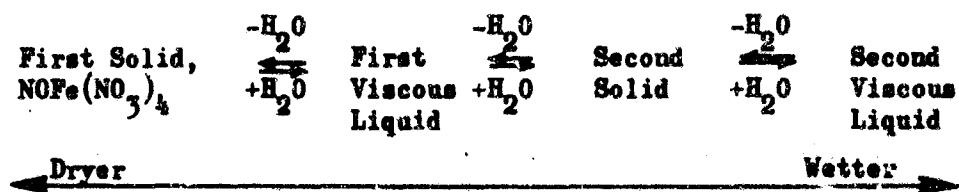
The iron content of the filter deposits far exceeded the aluminum or titanium content. However, this is not unreasonable if it is considered that the propellant loaded into the system was saturated with iron at ambient temperature. Thus, the solution of a small amount of additional complexed metal nitrate from the aluminum or titanium tank walls could produce a salting-out effect on the iron compound and yield a precipitate consisting mostly of $\text{NOFe}(\text{NO}_3)_4$. Also, the fittings and valves attached to the tanks were stainless steel and could have contributed a certain amount of additional iron corrosion products during the test period. This, however, would resemble the actual situation likely to exist in a missile system, where stainless-steel components would be intermixed with titanium or aluminum tanks. An unexplainable result of the analysis is the presence of aluminum in the titanium system and titanium in the aluminum system. It is possible that the filters were not sufficiently cleaned after the first analysis and that they were inadvertently switched when placed back in the flow system. In spite of this anomaly, the results do indicate that some corrosion of the aluminum and titanium tank walls did take place and contributed toward the occurrence of flow decay. It has not been proved whether enough aluminum or titanium would dissolve in completely iron-free propellant to cause flow decay deposits containing no iron.

CONCLUSIONS AND RECOMMENDATIONS

THE BASIC CHEMISTRY OF FLOW DECAY

Propellant-grade nitrogen tetroxide will corrode iron alloys (i.e., stainless steel) to a very, very small extent. This corrosion occurs regardless of the nature of the N_2O_4 ; it may be either brown (red) as specified by MIL-P-26539B or green (containing NO) as specified by MSC PPD-2A. The corrosion manifests itself as a few parts-per-million of iron dissolved in the N_2O_4 . Clogging of orifices by the redeposition of the iron material, in one form or another, is the phenomenon known as flow decay.

The form in which the deposited iron appears is a direct function of the water equivalent content of the propellant. At less than 0.1 percent (i.e., in essentially dry NO_2), a crystalline solid, $NOFe(NO_3)_4$, appears. At a higher water concentration, near the "use limit" of 0.2-percent water equivalent, the iron appears in a viscous or gel-like liquid phase. Other solids and liquids appear as the water content is increased to even higher levels. The equation below describes the behavior over the range of 0- to 0.5-percent water equivalent.



The chemical nature of the viscous liquids and the second solid are only tentatively defined. The first liquid phase may represent a partially hydrated (possibly monohydrate) ferric nitrate dissolved in concentrated HNO_2/HNO_3 , the second solid a higher (tri?) hydrate of ferric nitrate, and the second liquid phase this higher hydrate dissolved in the concentrated

acids. However, the overall chemical relationship of these materials is probably much more complex than this, involving numerous equilibria between the different deposits and all the various iron-containing species present in N_2O_4 .

It is therefore recommended that studies be undertaken to define the basic chemistry of the corrosion products of N_2O_4 in more detail. A clear definition of the chemistry of this system may allow for a solution to the problems of flow decay by some means that is not now evident or even inferable on the basis of the present limited knowledge.

PHYSICAL MANIFESTATIONS OF FLOW DECAY

Solubility of the iron species governs flow decay. Both the solid crystalline $NOFc(NO_3)_4$ and the viscous gel-like liquid phase have been shown to have positive temperature coefficients of solubility. Therefore, any N_2O_4 that has become saturated with its iron corrosion products is capable of depositing these corrosion products anywhere in the propulsion system if it encounters a lower temperature than that at which it was saturated. The saturation can be rapid (1 to 2 hours at 100 to 120 F), but may also be partly diffusion-controlled in large tanks, so that unless mixing of some types takes place, true equilibrium saturation may not always be achieved.

In a flowing N_2O_4 system, where there is a temperature drop (and the effect is magnified by a pressure drop, for reasons unknown) the iron materials will deposit and build up in small orifices and restrictions, thus impairing flow of the propellant. This is the manifestation called "flow decay".

If the propellant water equivalent is low, so that the solid crystalline $\text{NOFe}(\text{NO}_3)_4$ is deposited, buildup of deposits and flow decay occurs in needle valves, filters, and essentially any place where a small orifice is encountered. If the water equivalent is higher, so that the viscous liquid is deposited, flow decay has been encountered only in filters; needle valves are unaffected.

In the present study, the viscous liquid phase caused flow decay in filters with pore sizes ranging from 2-5 micron to 40-55 micron (nominal-absolute). Data from filters has been correlated in terms of the flow coefficient C_v , defined as

$$C_v = (\text{flowrate}) \sqrt{\frac{\text{liquid specific gravity}}{\text{pressure drop across filter}}}$$

and it has been shown that the smaller the initial C_v , the greater the probability of flow decay. However, anomalies exist in the data collected to date, and it is not possible to use the data to select a pore size and accurately compute the filter area necessary to handle some given volume of N_2O_4 without flow decay.

It is accordingly recommended that an extensive study of flow decay, as caused by liquid-phase deposits in filters, be undertaken. The objective of such work would be to develop a statistically reliable measure of flow decay as a function of filter parameters (C_v or other appropriate measurements), to provide design criteria for maintaining non-decaying N_2O_4 flow.

THE PREVENTION OF FLOW DECAY

Flow decay may be controlled by controlling temperature. Because both the solid $\text{NOFe}(\text{NO}_3)_4$ and the viscous liquid deposit have positive temperature coefficients of solubility in N_2O_4) flow decay can be

prevented by assuring that no temperature drops occur at any point in the N_2O_4 propulsion systems. In fact, it has been shown during this work that both $NOFe(NO_3)_4$ deposits and viscous liquid deposits can be redissolved by flowing hot N_2O_4 over them.

Application of this control method may be difficult or impractical on most missile systems; it would require either heating all lines and valves, or refrigerating the main tank.

Flow decay could be controlled by always maintaining the N_2O_4 at a water-equivalent level of 0.2 percent or more, and avoiding the use of small-pore filters. Under these conditions, the liquid phase deposit (which does not affect valve orifices) would be dominant, and this material would not clog a filter if the pore size and filter area were large enough. The previous recommendation relative to a study of filter parameters must be reemphasized, because the pore sizes and areas necessary to prevent flow decay in this manner are not yet known.

Flow decay could be controlled by always maintaining the N_2O_4 at a water equivalent of 0.1 percent or less, and developing a corrective additive to use in the N_2O_4 . At 0.1-percent water or less, ("dry" N_2O_4), the solid $NOFe(NO_3)_4$ precipitates, clogging either valves or filters. It has been shown that various organic additives can increase the solubility of $NOFe(NO_3)_4$ in N_2O_4 to the point where deposition and clogging will not occur, thus eliminating flow decay. However, to date, a completely satisfactory additive has not been developed. It is accordingly recommended that a concentrated effort be made to select and qualify an organic additive that can prevent flow decay in dry N_2O_4 without deleterious side effects.

In the present work, no additive was found that would eliminate flow decay arising from the gel-like liquid deposit. (Anomalously, dimethylsulfoxide appeared to dissolve deposits in laboratory tests,

but accentuated flow decay in the flow bench.) However, all additives tested thus far were selected on the basis of various theories about the viscous liquid phase, without real knowledge of the actual nature of the material. An additive might be selected if there were more facts on which to base such a selection, and accordingly, the earlier recommendation of studying and defining the basic chemistry of the liquid materials is reemphasized here.

In making these recommendations and suggested preventatives, it should be remembered that we probably have not yet have seen flow decay in all its possible manifestations. A single type of flow decay may only be one aspect of a problem that can vary in nature. An N_2O_4 propellant system containing iron corrosion products can exhibit phase changes of the corrosion deposits as a function of the normal operating temperatures experienced by a rocket propulsion system. Phase changes will also be experienced as a function of the ratio of total iron salts to the available water. The flow decay compound $NOFe(NO_3)_4$ has been shown to be a good dehydrating agent and it is presumed that those iron species containing small amounts of water will also be good dehydrating agents. Thus, it can be predicted that for a given tank of N_2O_4 having a relatively high water equivalent concentration (ca. 0.2 v/o), which would result in the formation of a gelatinous deposit, further corrosion will reduce the water equivalent concentration of the propellant such that crystalline $NOFe(NO_3)_4$ becomes stable in the propellant. Conversely, if propellant handling and transfer operations result in the addition of water to the system, the gel-like deposit may be converted to the second solid phase, a partially hydrated ferric nitrate.

PURIFICATION AND ANALYSIS OF NITROGEN TETROXIDE

Nitrogen tetroxide may be at least partially freed of $NOCl$ by treatment with silver nitrate. Because it has been suggested that chloride-free

N_2O_4 is not corrosive (and according to, if it did not attack iron and accumulate the soluble products, it would not cause flow decay) this approach should be investigated further.

It has been shown that the MSC-PPD-2A specification procedure for chloride analysis is unsatisfactory for accurate work at low chloride levels. A turbidometric method developed under this program has been shown to give much better results.

It has further been shown that the MIL-P-26539C specification method for water analysis, based on phase separation, is grossly inaccurate when the dissolved iron species are present in the N_2O_4 . The second liquid phase containing iron materials is not as soluble in N_2O_4 as is the liquid acid phase that appears in the absence of iron. Thus, separation will occur at a lower water level when iron is present, or, putting it another way, the phase separation method will give erroneously high results when iron is present. It is accordingly recommended that more accurate methods for analysis of the water equivalent in N_2O_4 be developed. Nuclear magnetic resonance has been used in the present work with some degree of success. It might also be possible to modify the phase separation technique to account for whatever level of iron might be present.

FLOW DECAY AND CORROSION OF NONFERROUS METALS

Preliminary data obtained during the course of this study indicate that N_2O_4 corrodes both aluminum and titanium to the extent that deposits containing these metals are detectable in filters. It is recommended that this study of other metals be extended to the point that it can be unequivocally determined whether or not flow decay is possible with nonferrous hardware.

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13. ABSTRACT
 Study of the phenomenon of flow decay, begun on earlier programs, was continued with a change to MSC PPD-2A propellant (N_2O_4 + 0.6 percent NO_2). Flow decay occurs with this propellant, even when dry (less than 0.1-percent water equivalent), as a result of deposits of the solid corrosion product, $NOFe(NO_3)_4$. It was found that the presence of excess water in amounts up to the general use limit of 0.2 percent changed the characteristics of the deposits formed when nitrogen tetroxide is heated, then cooled prior to or during flow. Instead of the crystalline solid ($NOFe(NO_3)_4$) which is deposited from dry propellant, gelatinous or viscous liquid phases are formed in wet propellant.

The appearance of these deposits is governed by an equilibrium solubility limit similar to that observed for the solid deposits in dry propellant. The gelatinous or viscous liquid deposits were not observed to adhere to and plug valves and orifices, as does $NOFe(NO_3)_4$, but they did clog filters. Chemical additives previously shown to be effective in dissolving and eliminating $NOFe(NO_3)_4$ were not effective against the deposits obtained from wet propellant. Traces of aluminum and titanium were detected in flow decay deposits obtained from flow systems with aluminum and titanium tanks.

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